The Application of Oils and Greases to Leather

BY

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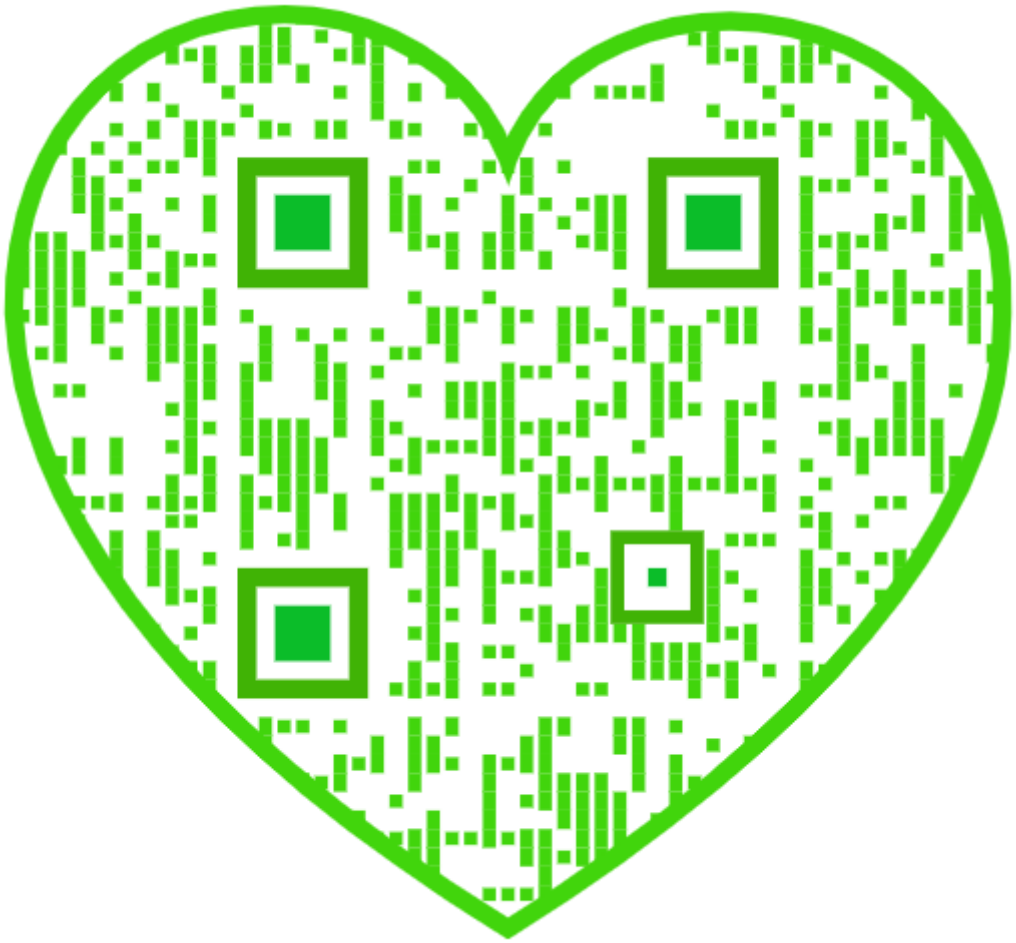

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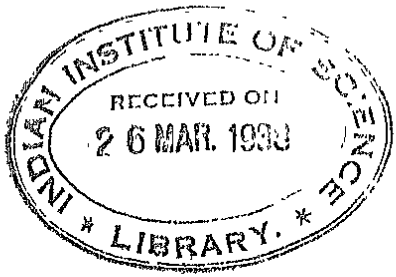

PREFACE

The object in compiling this volume is to present to the reader in compact and accessible form the available information regarding the application of oils and greases to leather. The use of oils and greases in the tannery is as old as the art of tanning, but in recent years the introduction of the chrome process has greatly complicated the matter. The literature of tanning is copious, but there is need of more highly specialized books dealing with the different phases of leather chemistry and practical tanning.

This volume will, we hope, fill this void in so far as the use of oils and greases is concerned. The matter has already been printed in serial form in the *Shoe and Leather Reporter,* but we have had many requests for the articles bound in permanent form so that they can be instantly available in every laboratory and tannery library.

The author, J. R. Blockey, M. Sc., is a recognized authority in the United States and Great Britain, and as far as we know this work is the only one published which gives the particulars of this important department of the leather manufacture.

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Application of Oils and Greases to Leather

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Application of Oils and Greases to Leather

Written by J. R. Blockey, M. Sc.,
for the Shoe and Leather Reporter.

The Economic Use of Greases

One of the recent developments of the war affecting the leather trade is the shortage of the common oils and greases used in leather dressing. This shortage has been a gradual growth but only recently has the question become acute. It has arisen partly from the shipping shortage but it is also due to the large quantities of oil which are used in the making of guns and more recently to the utilization of certain oils and greases (which have hitherto been regarded as industrial materials) for the production of food in the shape of artificial butter, lard and dripping. A large quantity of oils are also taken for the extraction of glycerine for the making of explosives. The extraction of glycerine does not, however, involve a complete removal of the oil (from which it is extracted) from the market. Most of the common oils such as cod, castor, whale, or what are called fixed oils, are composed of free fatty acids combined with glycerine. The oil may be regarded as a salt in the same way as common salt is the result of the combination between hydrochloric acid and soda.

$$NaOH+HCl=NaCl+H^2O$$

Caustic Soda. Hydrochloric Acid. Common Salt

Glycerine may be regarded as a base similar to caustic soda, except that its molecule contains three groups which can be replaced by the acid groups. $C^3H^5(OH)^3$ so that the salt of glycerine and hydrochloric acid would be $C^3H^5(OH)^3+3HCl=C^3H^5Cl^3+3H^2O$.

The true fats and oils are salts with glycerine as the base and fatty acids as the acid. For example the simplest type will be composed of one molecule of glycerine and three molecules of a fatty acid such as palmitic acid or stearic acid.

$$C^3H^5(OH)^3+3HC^{17}H^{35}C^{00}=C^3H^5(C^{17}H^{35}C^{00})^3+3H^2O$$

Glycerol. Stearic Acid. Stearin

Thus palm oil is approximately composed of $C^3H^5(C^{16}H^{31}O^2)^3$ which is called palmitin.

The differences between the common fixed oils and fats are due very largely to differences in the acid portion of the molecule. The acid portions of the mole-cule or the free fatty acids are themselves oily or greasy substances. The free fatty acid may be either liquid, pasty or solid. For instance, oleic acid is liquid and stearic acid solid. The original oil is called a triglyceride. The names are stearin, palmitin, olein, etc., and should not be confused with the commercial names spelt with an "e" such as stearine which may represent quite different substances. For instance, stearine represents several different materials, one of which is the free fatty acid from stearin, stearic acid.

The true oil or fat is therefore a compound of glycerol and a free fatty acid.

In the saponification of oils and fats to make soap and glycerine the process is briefly one of splitting the original glyceride into its two components, glycerol and free fatty acid. The saponification may be carried out by means of alkali so that instead of getting the free fatty acid itself the alkali salt of the fatty acid is obtsined.

For instance, in the saponification of stearin by means of caustic soda the products are glycerol and instead of stearic acid, its sodium salt, that is, sodium stearate.

$$C^3H^5(C^{17}H^{35}C^{00})^3+3N^aOH=C^3H^5(OH)^3+3C^{17}H^{35}C^{00}Na$$

Stearin. Glycerin. Sodium Stearate or Soap

The alkali salts of the fatty acids constitute the soaps. When soda either as caustic soda or as washing soda, has been used for saponifying the oil or fat the resulting soap is one of the usual hard soaps, and when potash has been used as saponifying agent, the soap produced is a soft one.

Bearing in mind this brief outline of the composition of oils and soaps we can go back to the sentence in the opening paragraph, in which it was stated that in the removal of the glycerol from the oils and fats, the whole of the oil was not removed from the market. The remaining portion of the oil, that is after the removal of the glycerol, may be placed in the market as soap or as free fatty acids. In the latter form they can be used as ordinary oils and greases, and this is one of the means which have been suggested to overcome the difficulty of the shortage of ordinary oils and greases.

Some of these fatty acids have been used quite successfully in leather dressing for many years past, for instance stearic acid is a white hard crystalline fat and is sold as stearin. This form of stearin must not be confused with other types of grease which are sold as stearine, e. g., wool grease stearine which is obtained by distilling crude wool grease with steam and separating the distillate into a liquid oleine and a solid stearine which may be pale yellow to brown in color and has a characteristic odor. It consists largely of free stearic and palmitic acids. Stearic acid itself is colorless and almost odorless and has been used for years as a constituent of drum stuffing mixtures.

Recently, owing to the great need of glycerol, other sources have been tapped so that many forms of free fatty acids are now

available for industrial purposes. Whale oil is now treated for the removal of its glycerol and the whale oil fatty acids is put on the market. This material is semi pastry and smells of fish oil. It is important that experiments should be conducted upon this material and means devised to utilize it in place of some of the ordinary oils. There seems no reason to doubt that it could be successfully used as a component of drum stuffing mixtures. If it is thought that the fatty acid will not have the same feeding properties on the leather fibres as the original oil it might be pointed out that in chamois leather making, in which the feeding properties or combining qualities of the oil are more necessary than in any other form of leather dressing, since the process is an actual oil tannage in which the oil actually combines with the fibre of the skin, in this case it has been proved that although cod oil and whale oils are almost invariably used, yet the effect is due to the fatty acid portion of the oil and that the effect produced in chamoising can be brought about by means of fatty acids alone.

Other fatty acids besides that from whale oil which are available and which are likely to be successful in leather dressing are the fatty acids of cod oil and castor oil. The most likely use for these materials is as constituents of drum stuffing mixtures and even as hand stuffing dubbins. In the former case, particularly when large quantities of grease are incorporated in the leather, the main factor of success is not so much the nature of the components of the mixture as the constituency. Some of the drum stuffing recipes which are often given in trade journals or kept as secret processes, may contain as many as five different materials. It is most likely that these recipes have been devised by purely empiric means or by accident and that a mixture of similar consistency but made from only two or at most three materials would be just as successful. It may be something like the fearsome recipes one comes across for seasons and finishings in which ten or twelve materials may figure, some of which may

be quite worthless and others may actually neutralize one another's effects.

It is certain that most of these new materials could be successfully used to replace some of the materials commonly used in drumstuffing but which are likely to be either very scarce or unobtainable. In order to be able to economize greases it will be a help to understand the objects of applying grease to leather and the function of the grease.

Origin of Application of Oils to Leather

In prehistoric times we know that men used skins of animals for clothing and it is very likely that the treatment which these skins received was one involving the use of oily substances. It would be found by constantly wearing a skin or a fur that the parts coming mostly into contact with the body would become in time the softest. The grease from the perspiration excreated by the body would become absorbed by the skin and by the constant bending backwards and forwards of the skin with gradual accumulation of grease from the body the skin would become soft, supple and strong. This was probably the origin of one of the esrliest methods of making leather, or of converting putrescible skins into something soft and permanent. The process would become a special one and instead of trusting to grease from the body, a special means would be adopted to incorporate the grease. It would not be a very distant step from the above to the process of smearing the skins with grease, obtained from the rest of the animal, and of bending and kneeding the skins so treated. One of the very earliest references to the art of tanning is actually a description of an oil tannage. It occurs in Homer's Iliad and compares the struggle between the Greeks and Trojans to "A man stretching a huge oxhide sodden or drunken with slippery lard."

It is therefore evident that the use of oils in leather making is a very ancient one and that a satisfactory leather can be

made by the use of them alone. Other methods of con skins into an imputrescible form were probably discove accident. For instance infusions of leaves and barks probably be found to have preservative properties. Skins be found lying in forest pools in which leaves and twigs an from trees would be rotting and such skins would be fo be more permanent than others.

This was probably the origin of the ordinary vegetab ning process. Knowing the effect of grease on the raw sl would not be long before the effect of grease on vegetable l was tried and found to be successful. Applied to skins had been immersed in infusions of leaves, etc., i. e., to veg tanned leather, it would be found that the resulting produ softer, more pliable and stronger than without the oil or g The early methods of converting skins into something mor manent, that is methods of tanning, had therefore, the objects as the modern process, although the latter are so plicated.

This short historical outline may serve as an introdu to the question of the aim of applying oil to leather an function of the oil.

The Function of the Oil

In the original process, which finds a very close parall the modern manufacture of chamois leather the oil was us an actual tanning agent with no other material necessar complete the tannage. In these cases the aim is an actual bination between the oil and the skin fibre. Only true oils o type already described are capable of being used in this This will include most animal (both marine and terrestrial) vegetable oils, and fats such as tallow, cod oil, olive oil, mi oils, could not be used for this purpose. The process is a s long one. The oil or fat is first applied liberally to the s nowadays in chamois leather dressing in faller stocks and

skins worked about very thoroughly. This forces the oil into the skins which are then hung up in a warm place. The oil undergoes a chemical change, which is accentuated by packing the warm skins in boxes or tubs. This treatment of applying oil, kneading, hanging up and packing in tubs may be repeated until the desired effect is obtained. The oil is split up during the process and some of the products of this splitting up combine with the skin fibre and produce the oil tannage. Part of the effect is certainly due to the formation of such substances as acrolein which is the cause of the penetrating smell produced in chamoising and which resembles formaldehyde. The proportions of the oils which are absorbed by the skin are removed either by pressing or washing and constitute degras and sod oil.

The chemical changes in the oil are only brought about slowly so that the process is not one of a few minutes or hours as is the case in the process of drum or hard stuffing.

The above is the object of the oil in a true oil tannage and of course only oils which are capable of undergoing such chemical change such as cod oil can be used for a straight oil tannage.

Mineral oils for instance undergo practically no change and are very resistant both to atmospheric and chemical influences.

The effect produced in a true oil tannage takes place to a certain extent in other processes in which oil is applied to leather but in which the oil is not the main "leathering agent." For instance in the oiling of the grain in tanned leather before drying a certain combination occurs between the oil and the leather. Similarly in stuffed leathers the amount of grease which can be removed is usually less than the amount which has actually been incorporated.

This effect therefore of an oil tannage or combination between the oil and the leather fibre occurs in most processes.

The Object of Oiling the Grain of Leather

Apart from the slight oil tannages just outlined, the object of applying a thin coat of oil to the grain of tanned leather in the wet state before drying out is to maintain a better color and also to produce a grain which will not crack on bending. This oiling of the grain is given to most leathers which do not receive a special process for incorporating grease. For instance, sole leather usually receives a light coat of cod oil before drying in order to lighten the color. It also makes the grain less liable to crack and allows a higher degree of polish to be given to the leather. This polish is obtained during the setting out, rolling and brushing processes and leather which has received a thin layer of oil on the surface, is much more highly receptive of smooth grain than leather without oil. Even leather which has to be curried, that is to be given a special process of incorporating grease, is usually given a coat of oil in the tanned state if the leather is to be dried out before being dressed. Thus split hide and dressing hides which are to be dried in the crust are usually given a coat of oil on the grain in the tanned state. Of course the leather is to be dressed at the same place as it is tanned there is not the same need to dry out the leather in the crust form and therefore no need to oil the grain. A very large proportion of leather is, however, tanned and dressed or curried at different places and in all these cases a coat of oil is applied before drying out. This will apply to vegetable calf skins, dressing hides, split hides and crust vegetable leather in general.

Improvement in Color

One of the main objects is to produce a better color. If two similar pieces of vegetable tanned leather were dried out, one coated with oil and the other without oil, without special care in the drying it would be found in nine cases out of ten that the oiled piece would be of better color than the other one. How does this arise? It is almost entirely a case of the surplus to

ning matter contained in the leather. In all processes of vegetable tanning more tanning matters are absorbed by the leather than are actually combined. This would be evident if leather were placed in clean water. Very soon the water would become colored caused by the diffusing out from the leather into the water of surplus or "unfixed" tanning matter. There is a certain proportion of this unfixed matter in all vegetable leather and it is this which causes an unoiled leather to be darker than an oiled leather, and the higher the amount of this unfixed matter in the leather the more pronounced is the difference between the color of oiled and unoiled leather and therefore the more urgent is the oiling of the grains. For instance, a sumach tanned sheepskin contains perhaps as little excess or unfixed tanning matter as any vegetable tanned leather, and this will dry out almost a perfect color without any oil. A lightly tanned dressing hide, say tanned largely in weak gambier liquors, contains rather more unfixed tannin than a sumach tanned sheepskin, and the effect of oiling the grain before drying, is rather pronounced, although by drying very careful it is possible to obtain a fairly good color. At the other extreme, take a heavily tanned sole or belting leather, which may contain up to 25 per cent of its total weight of unfixed or soluble tanning matter. If such leather were dried out without oil on the surface the effect on the color in most cases would be disastrous. The edges of the leather would be quite black and the grain quite irregular in color as well as being easily cracked in bending. How does the surplus or unfixed tannin affect the color so adversely, and how does oil on the grain improve the color? The best explanation would be obtained by the simple experiment of dipping one end of a long piece of filter or blotting paper in a tan liquor and leaving the upper end exposed to the air. Tan liquor would be drawn by capillary forces up the paper. Drying would take place and the upper portion of the paper would rapidly become dark and almost black. This is due to evaporation or drying

of the tan whilst exposed to air. Oxidation occurs and the color is darkened. A similar phenomenon occurs in the drying of leather containing excess of tan. The water evaporates from the surface and leaves a layer of tan which becomes oxidized and darkened. If water could be evaporated from the surface without bringing with it and depositing a layer of tan, that is if all the tan could be maintained in the interior of the leather and water alone evaporated from the surface, the color of the leather itself would be maintained. This is the function of the oil. By covering the clean wet grain surface of the leather with a film of oil, evaporation is retarded from that side and encouraged from the flesh side on the unoiled side, and the evaporation or drying which does take place from the grain side is not attended by the coming to the surface of surplus tanning matter which would be oxidized and darkened. The color of the actual grain of the leather itself is therefore obtained. This is the function of the oil in maintaining a good color when applied to the grain of wet tanned leather.

Effect of Oil on Tensile Strength and Preventing Crackiness

The tensile strength of leather is the resistance which the leather exerts against tearing or breaking when stretched. The crackiness of the grain is part of the same question. The strength of leather is measured by making a clean cut down the middle of a strip of the leather and by pulling the two adjacent ends in opposite directions until the leather either breaks or tears. This is done in a machine capable of measuring the pull exerted. The crackiness of course is not so capable of quantitative measurement but is usually merely tested by hand.

The effect of oil on these two things is very marked. If comparative pieces of leather be dried out, one with oil and one without measurements (either qualitative by hand or quantitative by machine) be made on the dried pieces it will be found

that the piled ones are much more resistant both to tearing and to cracking. With a lightly tanned dressing hide the effect is most marked even with a small dressing of oil. A great difference will also be noticed in the way in which the two leathers are cut by a knife. In one case the cutting is harsh and dry and in the other with the oil the cutting may best be described as "cheesey."

Quantitative measurements have been made of the effects of different amounts of grease and oil on different kinds of leather, only a summary of which can be given here. The effect of adding varying quantities of grease to tanned leathers is to increase the tensile strength. As the amount of grease is increased the tensile strength increases and as a general rule the higher the amount of grease the greater the tensil strength, other things being equal. The effect varies very considerably both as regards tannage and also the nature of the grease. Other things such as the amount of moisture in the leather also affect the question and it may be that in some processes where extra grease is corporated in the leather the amount of moisture may be reduced and the tensile strength reduced.

This increase in the tensile strength is due perhaps to two things, lubrication and separation of fibres. When the wet leather is dried in contact with oil the latter penetrates into the leather and coats the fibres with a film of oil and at the same time maintains the fibres in a very finely divided state. The effect of coating the fibre with a thin film of oil can be illustrated by intermeshing the fingers of both hands and trying to pull the hands apart. If the fingers be dipped in soap solution they will slide over one another much more readily. A similar thing occurs when the fibres are coated with oil. The fibres will then slide over one another much more readily without tearing, and this makes the leather much stronger and more pliable. The strain of tearing instead of being borne by isolated fibres is, in a way, passed on, so that the resistance is increased considerably.

The action of the oil in splitting up and separating the fibre bundles into the finest fibres will also operate in increasing the resistance to tearing. For these two purposes it is essential that the oil should be absorbed by the leather in a wet state. The effect is not at all the same if the dried out leather is oiled. The increase in the tensile strength is not at all appreciable compared with when the oil is applied to the wet leather. This fact of course renders the incorporation of the oil a much more difficult process than it otherwise would be. This might seem to be disproved by the so called dipping or burning in process in which dry leather is dipped in hot melted grease or oil or in which the liquid oil or grease is applied by hand to the dry leather. This method of incorporating grease in leather has other objects than increasing the tensile strength, and where it is applied without any other treatment the tensile strength is not markedly improved. But in most cases after the dipping process, i. e., after the dry leather has been immersed in and filled with the grease, the leather is subjected to treatment which makes this process more or less similar to other processes of incorporating grease. This treatment usually includes drumming or immersion of the leather in warm water so that both water and grease are present in the leather at the same time. In the final drying out of such leather the same process will occur as though the oil or grease had been applied to the wet leather so that the apparent paradox disappears.

The effect on the color is in the same category as that on the tensile strength. If the oil be applied to the dry leather instead of improving the color, it will be darkened. This will be caused by the lack of preventing the accumulation and darkening of tan on the surface and also by the actual darkening effect of the oil itself. By applying oil to the grain of the dry leather instead of penetrating throughout the leather it will remain on the surface and produce the same effect as oil will stay on a piece of paper or cloth. This is not due to the actual coloring matter in

the oil and not a strain in the real meaning of the term but is due to the effect on light reflection.

When a spot of oil is placed on white paper the darkening is due to the reduced reflection of light. Instead of having a rough surface which reflects a large proportion of the light falling upon it this film of oil only presents a smooth surface. The area of the surface is very much reduced and the light instead of being reflected is largely absorbed.

The effect of the area of surface on the amount of light reflected and on the color of a substance may be illustrated by a crystal of chrome alum. A large crystal of chrome alum will appear almost black but by grinding it to varying stages of fineness of division the powder will appear almost white. It is a similar effect which makes an oily surface dark.

When therefore oil is applied to leather to improve the color, it is applied to the wet leather so that it is absorbed and penetrates the leather.

In the after treatment of leather which has been stuffed by dipping, already briefly mentioned, one of the changes that will occur is that the film of oil or grease on the surface is broken and therefore made to reflect more light.

This is achieved by drumming and the action of the water. When a piece of leather, which is dark colored through the presence of grease on the surface, is sharply bent it usually results in lightening of the color particularly if the darkness is due to a solid grease and not to liquid oil. In this case the bending of the leather breaks up the grease on the surface.

Similarly if the grease from the surface be removed by a solvent the color will be lightened.

The question of color is a very important one in many leathers which are stuffed and it is dependent upon the factors just outlined. It is not always the amount of grease in a leather which makes it dark or light. A leather containing little grease may be darker than one containing much grease. The color is

due to the presence or absence of a film of oil on the surface and to the fineness of division of the oil or grease at the surface.

A word might here be said of the effect of the color of the oil on the leather. Consider for example the color of mineral oils. This may vary from a light clear transparent colorless oil to a dark green oil transparent in thin films.

It is often thought that the lighter the oil the lighter will be the leather to which it is applied but this is only true within very narrow limits. If the two extremes of mineral oil are taken and applied to wet leather and the leather dried out the difference in color of the final leather will be almost inappreciable.

The oils will have penetrated the leather and will not have left a film on the surface. Of course it is possible for oils themselves to contain coloring matter and the use of such would darken the color. Inferior qualities of cod oil may also cause stains, but these are usually in streaks of darkened color. The streaks are not due so much to coloring matter in the oil but to the fact that the oil is not quite homogeneous. The streakiness is most apparent when the oil has more than a fair proportion of foots (the semi solid deposit which separates to the bottom of the oil), the amount of which increases as the temperature falls and vice versa diminishes as the temperature rises. If such an oil be applied to the surface of leather (and it is only in such cases and not in drum stuffing that the streaks are noticeable) it may be quite tepid when applied but the foots may separate out before the leather is dry or before the oil has penetrated and so leave an excessive amount in certain places thus, causing streakiness.

That the improvement of tensile strength is not due to lubrication alone as is sometimes thought is proved by removing the grease. This if leather be curried and then the grease removed and the tensile strength of the leather be measured (1) before currying, (2) after currying, (3) after removal of

the grease, it will be found that the tensile strength of the leather after removal of grease is higher than the original leather although of course not as high as the leather with the grease in. This shows that some other factor besides lubrication plays a part in increasing the tensile strength. This other factor is either the increased separation of the fibres or an actual oil tannage.

Prevention of Crackiness

On bending leather, grain outwards, it is often found that the grain opens or cracks. This method is often applied as a test of quality. For leather which will be subjected in usage to a bending strain the test is of course essential. For instance in leather for boot uppers it would be fatal to have a leather which would crack when bent. But in many cases the test is applied to leather which is not subject to bending and in which the value of the test is not easy to determine. For example in sole leather it is not easy to see what relation there is between crackiness and wear. The boot sole is never likely to be bent so much that a crack would develop, but in most cases the aim is to produce a leather which will not crack.

One of the main methods by which this aim is achieved is by the application of oil to the leather, either to the surface or by a more complete impregnation. The effect is the same as that described in connection with tensile strength, that is, the resistance to crackiness, like the resistance to tearing, is increased by the incorporation of oil and grease. In the same way also must the oil be applied to the wet leather in order to increase the resistance to cracking. If a piece of leather which cracks on bending be taken and oiled on the surface whilst the leather is wet and then dried out and finally the grease removed from the dried leather it will be found that the final leather may not crack at all or at any rate not so easily as the original leather but more easily than before the removal of the grease. The effect is there-

fore similar to that which causes the increased tensile strength and is due to two things, the lubrication and the separation of the fibres by means of the oil. It is not difficult to connect the two things and to see that the question of cracky grain is largely one of tensile strength, not so much of the whole leather as of that near the surface. Two or three factors govern the crackiness of leather besides the question of tensile strength or of presence of grease.

Effect of Thickness of Leather on Crackiness

One of the factors is the thickness of the leather. It is obvious that the stouter the leather the bigger is the strain which the outside of the leather has to withstand when the leather is bent. The dislocation or stretch of the surface of the leather and the tendency to crack are much greater when the leather is thick. Contrast the relative strains imposed upon the grains of a piece of stout sole leather and a skiver when bent double.

This should be borne in mind when comparing leathers of different thicknesses and seems a strong argument against applying the test of crackiness to such leathers as for sole purposes.

Effect of Moisture on Crackiness

Nothing affects the ease or otherwise with which a leather creaks on bending as the amount of moisture contained in the leather although the point is often overlooked, particularly by buyers of leather. Many leathers which in the ordinary condition are quite free from cracks would if dried, crack very easily. In fact very few leathers would not crack at all if the leather was completely dry. (It might be pointed out that ordinary vegetable tanned dry leather may contain anything from 10 to 20 per cent of moisture whilst chrome leather usually contains rather less.) The effect on the leather of removing a portion of this moisture is very marked. It is, however, extremely difficult

to remove all the moisture requiring many hours at a temperature of boiling water. In the ordinary conditions of a tannery it is not possible to remove more than a small portion of this moisture, and even in the hottest drying rooms or stoves the amount of moisture left in the leather is usually as much as ten per cent. The expressions which are used in tannery practice to describe dryness such as "bone dry" are therefore only relative and not absolute.

The moisture naturally present in the leather plays a very important part. Without it the leather would be much harder and would, to use a tanner's expression, have had the nature taken out of it. One of the most marked effects is on the tendency to crack. By removing a very small proportion of this contained moisture the surface of the leather becomes more brittle. A very small difference in the amount of moisture may produce a very marked effect on the tendency to crack. Thus it is sometimes the case that leather as it is finished that is as it comes from the final drying rooms may crack quite easily, but by leaving it in the warehouse, that is in a cooler and more moisture laden atmosphere it slowly absorbs moisture and the tendency to crack may disappear entirely.

One method of removing the tendency to crack which is often adopted is that of buffing. By removing a very thin shaving from the grain of the leather, it is often possible to prevent cracking or opening of the grain.

Hand Stuffing

So far only the method of applying oil to the surface of wet leather has been dealt with although other methods have been mentioned. The method which comes most closely in principle and in effect to the method of oiling the grain is that of hand stuffing. This differs from the oiling of the surface of the leather merely in the point that instead of liquid oil a paste or dubbin is applied. This dubbin is made from a solid fat and a

liquid oil, for example the commonest of all dubbins is composed of approximately equal parts of cod oil and tallow. By melting the tallow and adding the cod oil thereto and then allowing the mixture to cool with repeated stirring a pasty, almost homogeneous mass results. This is a type of the materials which are used in hard stuffing. As before, the grease must be applied to the wet leather. This is carried out on tables, the workman having the leather before him with the dubbin on one side. The dubbin is taken up by means of a brush and brushed on to the surface of the leather as evenly and as smoothly as possible giving certain parts rather more of the mixture if necessary. The leather is then hung up to dry. The whole of the grease does not penetrate into the leather as in oiling off. Only the liquid portion of the dubbin penetrates leaving the harder portion on the outside. When the leather is sufficiently dry and when the oily portion has penetrated the stiff portion of the grease remaining on the surface of the leather is then removed by slicking off. In principle, the process varies very little from that of oil. It differs, however, in this important respect, that the amount of oil which can be incorporated by one application is so much higher in hand stuffing than in oiling. By making the oil in a paste form a much larger quantity of it can be held to the surface of the leather than when applied in liquid form. Instead of running off as it would if too much liquid oil were applied and the leather then hung up, the paste adheres to the surface and as the leather dries the oil is gradually absorbed from the dubbin. This method, therefore, is applied where it is required to incorporate more grease than by oiling only. For example, it is not used for sole leather where the object of the oil is mainly to give improved color but is used for such leathers as harness and belting. By this process only liquid oils are absorbed by the leather, so that the amount of oil which can be incorporated by the leather without the latter feeling or appearing greasy is strictly limited, for it should be obvious that if a solid grease could be

taken up by the leather it would be possible to have much larger quantities in the leather without producing greasiness than when liquid oil alone is used.

The same factories play a part in hand stuffing as in oiling in the production of increased tensile strength. As it is used for harness and belting the question of color does not always arise and the improvement in the color by hand stuffing is not so prominent as by oiling. This is due to the fact that more grease is absorbed and that the surface of the leather may be very rich in oil which prevents the lightest possible color from being obtained by the effect on light reflection as already described. The darker color is due not to the leather itself or to the tanning matter on the surface but to the presence of a film of oil. Since more oil is absorbed the effect on the tensile strength is also more pronounced and, therefore, the method is used for such purposes as belting and harness leather where tensile strength is a prime consideration. Where extra amounts of oil are derived in the leather, the dubbin may be applied to both sides but this, of course, retards the drying considerably.

The dubbins are always composed of liquid and solid fats. The function of the oily portion has already been described. The part which the harder portions play e. g. the tallow in the ordinary cod oil-tallow dubbin is really a subsidiary one. Very little of the tallow itself actually penetrates the leather. Its main function is to serve as a stiffening medium for the cod oil so that a larger amount of oil can be held in contact with the leather than would otherwise be possible. If the tallow contains any liquid portion this will, of course, be absorbed by the leather. If the tallow merely serves as a stiffening medium it might be thought possible to use it over and over again. It is not, however, often wise or possible to do this, it is much better to discard the table grease (the grease removed by slicking off the harder scaly portion) for hand stuffing purposes and to utilize it for drum stuffing or other purposes. Changes occur in the tallow,

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for instance, it becomes much darker in color and cannot satisfactorily be used over and over again although it is quite feasible to use it two or three times.

Hitherto there has been great prejudice against using any other materials than cod oil and tallow for hand stuffing but it is quite possible to use other materials successfully and with the present shortage of oils and greases it may be necessary to devise new mixtures. That the tallow is not essential can be proved by using any other material which will serve as a stiffner for the oil. For example, a paste can be made of cod oil and some other material such as French chalk which can be applied quite successfully as a hand stuffing dubbin. In such a case the oil leaves the chalk on the surface and this can then be removed almost unchanged. All that is really essential is that the two materials should form a homogeneous paste which will adhere to the surface of the leather and that one of the materials should be liquid and the other solid. A mere homogeneous paste alone is not sufficient, thus vaseline or petroleum jelly which is quite homogeneous and smooth can be applied to the leather as a paste but it does not split into two components, the liquid penetrating the leather and the solid remaining behind. If an attempt were made to hand stuff with vaseline alone the resulting product would be unsatisfactory, very little oil or grease would have penetrated the leather and there would be left on the surface a greasy mass instead of a hard portion capable of being removed by the slicker leaving the grain clear and free from grease.

Hand stuffing has one advantage over other methods of incorporating grease and that is that the amount of grease can be varied in different parts of the leather. For example, in a piece of leather which is very uneven in substance the thick parts will require more grease than the thin parts to make a uniform result. This can easily be achieved by putting a thicker layer of dubbin on the stout places. A skilled man knows how to regulate the amount of dubbin on various parts of the leather to

allow for various substances and different degrees of softness in the finished leather. The disadvantages are that the process is very slow and that the amount of grease which can be incorporated is low compared with the methods of drum stuffing. When leather is to be sold by weight the latter point is of great moment.

Drum Stuffing

This method differs in principle from those of oiling and hand stuffing. It is in fact a modification of the process adopted in early times of forcing greases into leather which was mentioned at the beginning of this article and which is similar to the modern method of oil tannage as illustrated by chamois leather manufacturing.

The method in outline consists of churning the damp leather in a drum along with oil instead of applying the oil to the wet leather and then drying out so that the grease penetrates as the leather dries, a process which may take days. The grease is actually forced into the leather in a few minutes without the assistance of drying. The stoutest leather can be drumstuffed in half an hour.

It is very rarely that liquid oil alone is used for this purpose, because this could be incorporated by the leather quite easily by other means, either by oiling the surface or by the process of fatliquoring which has yet to be described.

Drum stuffing is almost invariably used where it is desired to incorporate in the leather not liquid oil but something much harder. The grease taken up may vary from a substance which is almost liquid to a very hard wax (at ordinary atmospheric temperatures). This of course cannot be achieved cold and it is the use of heat which distinguishes the process so much from those already described. Before the grease or wax is taken up by the leather it must first be liquid. By drum stuffing, grease may be taken up which at ordinary temperature is solid, it is this possibility of incorporating solid greases that opens up such

wide modifications. It is obvious that if a grease, which is solid, can be absorbed by leather a very much larger quantity can be taken up without the leather becoming greasy (to the feel or appearance) than if liquid oil were absorbed.

Outline of Method of Drum Stuffing

As already mentioned the use of heat is necessary in drum stuffing. It is therefore necessary to use some means of applying the hot melted grease to the leather. This is achieved by special drums which are shaped like ordinary tanning drums, but differ in the fact that there are means of warming the drum. This is done by driving hot air through. A special apparatus is attached to the side of the drum consisting of steam pipes over which air is drawn by means of a fan and driven into the drum through the axle. By regulating the steam pressure it is possible to vary the temperature of the drum from atmospheric temperature almost to that of boiling water. Very often in addition to the hot air apparatus it is possible to blow live steam into the drum. This is a more rapid method of warming up the drum, but is not often used whilst the leather is in the drum. Steam is usually only blown into the drum before stuffing to heat the drum itself. Having made the drum warm the leather is then entered and the drum turned for a short time (10 to 20 minutes) with the hot air going through. This is to warm the leather to the desired temperature before the grease is put into the drum. Otherwise if the melted grease were poured into the drum before the leather was hot enough the grease would be congealed. When the leather is sufficiently warm (and this can be indicated by a traveling thermometer, that is, a thermometer with its bulb inside the drum, but with its index scale visible from the outside) the melted grease is added through the axle whilst the leather is being turned. The grease is previously melted to the desired temperature by heating in steam-heated jacketed pans. The drum containing the leather along with the

melted grease is turned for another half hour or so, when if the work has been satisfactorily carried out and the conditions correct, the grease will have been all taken up by the leather. If the grease has not been properly taken up the drumming is continued. The leather may then be removed from the drum and proceed to the next process, although many drum stuffers prefer to run the leather for a time either with the door off, or where this is not possible, by blowing cold air through. (In drums with the door in one of the ends, that is one of the flat surfaces, it is possible to run with the door off, but in drums with the door in the periphery it is not possible.)

This extra turning allows the leather to cool somewhat and often allows any surplus grease to be absorbed. This further absorption may be due to contraction of the grease in the leather produced by cooling or to a slight drying action caused by change of air.

The above is a brief outline of the usual methods of drum stuffing the details of which may vary very considerably. Such things as temperature of stuffing, amount and nature of the stuffing greases, the condition of the leather as regards moisture; the previous history and treatment of the leather all play an important part in the success and effects of drum stuffing.

There is one other method of drum stuffing which is sometimes practiced, more especially on the continent and which is worth a brief mention. This consists of applying the grease to the leather on the table and then drumming the plastered leather in a heated drum until the grease has all been absorbed. It is usually claimed that this method gives the leather a better color than when stuffed in the usual way but it is probably due to the fact that a good deal less grease is taken up by the leather in this way. The method certainly has nothing to recommend it from the point of view of simplicity or saving of time and when high yields are desired it cannot be compared with the more usual

plan of warming the leather in the drum and then running in the melted grease through the axle.

Influence of Temperature in Stuffing

Obviously the temperature must be high enough for the stuffing greases to be melted. If the latter is only past it will be impossible to drum in the whole of the grease. Only the liquid portion will be absorbed. The temperature is therefore based partly upon the melting point of the grease and must be at least at such a point that the whole of the grease is liquid. As the temperature at which greases melt varies very much it follows that the temperature of stuffing may vary. It is also obvious that the more fluid the melted grease is the more readily will it be absorbed, and the higher the temperature the more fluid is the grease. There are, however, limits to the temperature which can safely be used, the effect on the leather being the determining factor. Leather will not withstand too high a temperature. As the temperature is raised the leather will begin at a certain point to show signs of burning or scalding such as curling and shrinking. The temperature at which the leather begins to be adversely affected depends upon the kind of leather, tannage, amount of moisture contained therein, etc. Some tannages are much more resistant to high temperatures than others Thus, taking the case of vegetable tanned leather first, most leather will withstand a temperature of 120 degrees F whilst some will be slightly scalded at 150 degrees F and the majority of well-tanned leathers only begin to perish at 160 degrees F These are all in the wet state. Dry leather will withstand much higher temperature than the same leather in the wet state and the drier the leather the more resistant it is to heat. As the leather has to be stuffed wet the temperature at which the leather is safe must not be measured on the dry leather. As some greases are only really fluid at higher temperature than those at which the leather begins to perish they cannot be used in drum

stuffing. It is for this reason that the process of dipping the dry leather in melted grease is sometimes adopted, when it is desired to incorporate in the leather a very hard grease of high melting point, that is a grease that could not safely be incorporated by drum stuffing. This point of dryness will be referred to again when dealing with the process of burning in or dipping.

The extent to which the leather has been tanned also has an influence on the effect of temperature. A leather which is under tanned or too lightly tanned, will not withstand such a high temperature as a well-tanned leather. This is particularly the case when the leather has an undertanned or raw streak in the center. The outside well-tanned portions will be safe, but the inner portion will be ruined at a much lower temperature than would otherwise be safe. The effect of this on the unfinished leather may not be very apparent to the eye, but the tensile strength of the leather as a whole will be lowered and if a section be cut it will be found that the centre shows signs of scalding.

It is sometimes said that an overtanned leather will not withstand as high a temperature as a merely well tanned leather, but this is probably due to the fact that an overtanned leather has usually been tanned without as much care as and also more quickly than a reasonably well tanned leather.

Chrome tanned leather will withstand a very much higher temperature than vegetable tanned leather, both in the wet and in the dry state. For instance, well tanned chrome leather can be boiled in water without the fibres being destroyed.

This allows much higher temperature to be used when stuffing chrome leather than vegetable leather and consequently much harder and higher melting point greases can be used.

When stuffing chrome leather it is quite possible to go up to temperatures just below the boiling point of water. (A temperature higher than boiling point 212 F. obviously cannot be used when stuffing wet leather, for at this temperature the water in the leather would boil.)

It is usually the aim in drum stuffing to use as low a temperature as will enable the grease to be absorbed. The higher the temperature the more easily will the grease be absorbed, but it may have an adverse effect upon the color of the leather. When stuffing leather which is desired of good or light color the temperature should be lower than when stuffing leather which is to be black or in which color is not important. It is, however, possible to defeat one's object if the temperature is too low, for in this case it may result in the grease being too viscous to penetrate properly, or whilst saving the color of the leather itself the effect of unabsorbed oil or grease may be to darken the leather.

Amount of Moisture in the Leather

Perhaps the thing which is most important in drum stuffing which is most often the cause of faulty stuffing is the amount of moisture contained in the leather. It has already been explained in connection with the application of oil to the surface of leather that the grease should be absorbed by the leather whilst the leather is in a damp state. This is to ensure that the fibres shall be separated and coated with the oil so as to produce increased tensile strength and good color. The drier the leather is the more readily will the grease penetrate. This is only what might be expected. In the dry leather the spaces between the fibres are much larger than in the wet leather. Moreover the water in the leather exerts a repelling action on the oil in the usual way in which oil and water will not "mix." There is a temptation therefore to have the lesther too dry in order to ensure that the whole of the grease shall be absorbed. If the leather is too dry the oil or grease may be taken up but the effect on the color is to make it dark and irregular. Whilst this would not matter if it were a case of dark or black leather, the effect of having the leather too dry is also to produce a leather lacking in tensile strength and suppleness. It will produce an ill-nourished leather. The amount of moisture in the leather must be very

closely watched and controlled. It would not be possible to make the grease penetrate if the leather were as wet as possible, say as wet as when first removed from the tan liquors. Very little gresse would be absorbed under these conditions. The leather must be dried somewhat before stuffing. This can be achieved either by squeezing or pressing out some of the moisture or by hanging up to dry. The exact point at which the drying should be stopped is a matter of experience and cannot very well be described in words. With undyed leather a great deal can be told by appearance and color, the color becoming lighter as the leather dries. With dark colored leathers it is not so easy to determine the correct point and the color test cannot be applied. One way, of course, would be to calculate the amount of moisture on the weight of the original wet leather before drying.

Drying

If the leather be in regular lots it can be assumed that the amount of moisture in a given number should be always the same, so it is possible to dry the leather until equal numbers weigh the same. Having determined just exactly the best point on a given lot with regard to moisture content for stuffing, it is possible to take the weight of this lot as standard and to dry all subsequent lots to such a point that the weight is the same as the standard. This would entail a tremendous lot of taking down, weighing and hanging up again when the drying is carried out by hanging. If the drying be carried out by means of a press or squeezing machine, it is possible to regulate the amount of moisture squeezed out by regulating the pressure. This is, therefore, one great advantage of drying machine over drying by evaporation, that is by drying in the air. Another advantage is that of speed. The process of squeezing liquid water from leather is much more rapid than removing water by evaporation. Thus, if the leather is passed through a squeezing machine it may take less than one minute to pass one piece of leather

through, whilst to remove the same amount of moisture by evaporation would take hours. There is, therefore, a great saving of time and also of floor space. When squeezing in a press whole packs of goods are squeezed together instead of individually as by a squeezing machine. There is an even greater saving of time. The amount of moisture removed by a press is also more under control than by a squeezing machine, the pressure being more easily and exactly regulated. In a press also the goods are most evenly dried. The pressure is uniformly exerted throughout the whole pack so that no parts are more squeezed or dried further than others, as may be the case to some extent when passed through a squeezing machine and as is the case to a very marked extent when drying in the air. By passing singly through a squeezing machine the leather being of uneven substance and texture becomes subjected to the greatest pressure at the thickest places.

By drying in the air by evaporation the drying is most uneven, since the drying capacity of the atmosphere varies very much. Thin places in the leather will tend to dry most readily; exposed places will also dry more easily than places which have not such free access to the air and when the air circuation is fairly free. When drying by evaporation very great care must be taken to make the drying as uniform as possible, not only throughout one lot but also in successive lots.

The three advantages of machine drying over air drying are therefore:

(1) Drying is under control and can be regulated.

(2) Drying is more rapid and space is economized.

(3) Drying is more uniform and it is much easier to dry successive lots to the same extent.

Certain disadvantages of drying by pressing or squeezing are sometimes advanced by curriers. In drying by air the fibres are supposed to remain more apart than when squeezed, the pressing action of the latter is said to make the fibres coalesce

together and to make the leather thinner and flatter. This is supposed to make penetration of the grease more difficult and to make a final leather lacking the substance of leather which has been dried by evaporation. On the other hand it is also urged that if the leather is compressed by squeezing, it will, by the turning action of the drum, again swell and have its fibres separated so that the final leather has good substance. By careful drying by both sets of processes there is not likely to be any marked difference.

When the leather has been through the squeezing or pressing machine it may even still be too wet for stuffing and in this case the drying must be continued by evaporation in the air.

In fairness it ought to be stated that most of the disadvantages which have just been urged against drying by evaporation, are avoided in the modern systems of evaporation. Certain types of drying machines (by evaporation and not by squeezing) will enable leather to be dried evenly as well as quickly. By being able to regulate the temperature of the air in the drying machine and also the rate of change of atmosphere, both of which are possible in modern drying machines, the drying of the leather is under perfect control and it is possible to dry evenly rapidly and to any given degree of moisture.

One rough test which curriers often apply to determine if the leather to be stuffed contains sufficient moisture is to bend the leather in a double fold and to observe the formation of beads of moisture which the squeezing forces to the surface. These beads should not appear too readily but if they do not appear at all the leather is too dry.

Bearing in mind what has been already said about the influence of moisture upon the ease with which the grease will penetrate the leather it is obvious that by varying the amount of moisture in different parts of the leather the amounts of grease which are taken up by those different parts can also be regulated. This is of immense importance in successful drumstuffing.

Leather is not of uniform thickness and texture and if the same treatment be given to all the parts the final result will not be perfectly uniform. This is one reason why the tanning and dressing of leather is so much more difficult than, say, the finishing of cloth. Some of the main variations in leather are softness, substance, texture, looseness or tightness of texture. For example, in a whole hide the butt is the firmest and its texture is the closest. Parts of the shoulder may be the thickest but the texture is spongy, whilst the flanks are the thinnest, softest and loosest. This is why hides are usually rounded into several parts either before tanning or dressing. With smaller skins such as goat and sheep which are too small to cut up into sections, the difference in texture in the finished skin is very noticeable and some of the parts are usually rejected or used up for an inferior purpose. For instance, with box calf for shoe leather, the flanks are too poor and loose often to be made into the outside of a shoe, and they may, therefore, be cut out and made into tongues.

For drum stuffing modifications may be made during the process to overcome to some extent the inequalities of the leather.

Varying the amount of moisture in the leather is one of the best means of producing even uniform results. The parts of the leather which would be softest (without different treatment) such as the flanks and the bellies are made wetter than the other parts. Any part which is soft enough without much grease or which would be too soft with the average amount of grease is made wetter than the other parts before stuffing. These wet places do not absorb as much grease as the dry places and so the tendency to over softness is avoided. Similarly the thinnest parts of the leather quite apart from the amount of moisture contained will absorb the grease more rapidly than the thicker places so that it is usual to make the thin parts wetter than the thick parts.

With leather which has been through a press, the amount of

moisture is regular throughout, and the leather is usually too wet to allow any further wetting of the thin places. It is sometimes, therefore, the plan to take the pressed goods and hang up to dry in the air for a short time and then to wet back the thinner places. With leather which has been dried by evaporation, the thin places can be damped during the drying or the drying can be carried to excess and then the thin places damped again.

Leather is often dried out completely before stuffing and then damped back again. Curriers, for instance, often buy leather in the crust form ready for stuffing. In these cases the leather may be damped back by immersing the whole piece in tepid water and something can be done in this way to give the thick places more water than the thin places. In the other cases the extra water is given by means of brushes by a sprinkling or spraying action.

Advantages of Drumstuffing

An outline of the usual method of drumstuffing and of the factors that govern the absorption by the grease has now been given. It remains to discuss the advantages which this process has over the older methods of hand stuffing.

(1) Speed. The length of time required to drum stuff a pack of goods is much shorter than to hand stuff the same pack. Instance of having to treat each piece of leather singly 40 or 50 pieces may be stuffed together in the drum. The amount of labor required also is much less. In hand stuffing, each piece of leather is handled several times for spreading on the dubbin, hanging up, setting out by hand, restuffing or oiling, whilst in drum stuffing the leather has only to be placed in the drum and taken out again.

(2) Uniformity and Ease of Control. If the leather is uniformly moist the amount of grease absorbed will also be uniform, each piece of leather taking an equal share of the total

amount of grease. In hand stuffing, on the other hand, it requires great skill to regulate the amount of grease which shall be taken up. In a similar way the control of the process is much easier. It is possible to regulate exactly the amount of grease which is put in the drum for a given amount of leather so that not only is uniformity possible in the leather of one lot but successive lots also can be made quite alike.

(3) Economy. In hand stuffing only a portion of the dubbin is absorbed and the harder parts have to be removed by sliekers. This cannot be used over again many times so that a large proportion of the original grease is wasted. It is of course not completely wasted since it is possible to use it over again for chesper elasses of goods, and in fact it is usually used up by adding it to drum stuffing mixture.

Apart from the waste of grease in this way there is usually an economy in drum stuffing in what eheaper greases can be used. The commonest mixture used for hand stuffing is made from tallow and cod oil both of which are expensive compared with the oils and greases which can he used for drum stuffing. Of thess two materials it is usually thought essential to use only the very best qualities for hand stuffing whilst for drum stuffing it is not so essential. The penetration of the grease can be made so complete in the leather proeess that there is not the same fear of producing stains as in hand stuffing.

This advantage of using cheaper greases in drum stuffing is however usually offset by the faet that much larger quantities of grease are absorbed than in hand stuffing.

(4) Weight. None of the previous advantages is, however responsible for the popularity of the drum stuffing proeess and for its gradual ousting of the older proeess so much as the advantage of being to incorporate much larger quantities of grease. This arises from the faet that much harder gresses can be absorbed by drum stuffing than by hand stuffing, since the proeess is used in conjunetion with heat, any grease can be used

which is fluid at a temperature lower than at which the leather would be destroyed. By being allowed to use harder grease it is possible to incorporate much larger quantities without the leather appearing greasy. The harder the grease the more of it can be taken up by the leather without producing a greasy feel or appearance. In hand stuffing it is not often possible to incorporate more oil than 10 to 15 per cent without the leather being dark colored and both feeling and looking greasy. In drum stuffing on the other hand it is possible to incorporate amounts up to 25 per cent and produce a dry feeling leather. These percentages refer to the amount of grease in the final dry leather and must not be compared with the figures sometimes used by currriers based on the weight of grease compared with the weight of the original leather. For instance a currier sometimes says he has got 50 per cent of grease in his leather. He means that 100 parts of original leather have absorbed 50 parts of grease, but the final leather only contains 50 parts of grease in 150 parts of leather or 33 1-3 per cent. The factors which govern the amount of grease which can be got into leather are (1) preliminary treatment and condition of the leather, (2) specific gravity of the stuffing grease, (3) hardness of the grease.

Preliminary Treatment and Condition of the Leather

(1) The more compact a leather is, that is, the closer together the fibres, before stuffing, the less the grease that can be absorbed. On the other hand if the leather be very open and spongy, and the fibres very separated, the more grease can be taken up. Thus a leather which is over-tanned or loaded with extract or weighing material will not absorb as much grease as a merely well-tanned leather. An undertanned leather also will not absorb as much grease as a well tanned leather.

A leather which has been heavily rolled, or set out, or squeezed immediately before stuffing may be made more compact and so capable of absorbing less grease, but it should be borne

in mind that by the churning action of the drum the effect of the squeezing or compressing action may be largely overcome. This applies only to drum stuffing and not to dipping.

(2) The higher the specific gravity of the grease, that is, the more weight there is in a given volume, the higher will be the weight of the leather which can be obtained assuming other things to be equal. Thus, to take an extreme case, if the volume of the space to be filled by the grease is the same in two cases, and in one case the specific gravity of the grease be 0.75 and in the other 1.00 the former will only take up ¾ as much weight of grease as the latter. The variations in the specific gravity of the common oils and greases are not large, varying little more than 0.1 from 0.850 and may not appear very significant but when taken into account the total amount of grease used, say, in a week, the difference may be very appreciable. This is a point usually lost sight of, but it is one which may play a prominent part at the end of a year and one which can be very easily controlled. The measurement of the specific gravity of the component parts or of the stuffing mixture themselves may be very quickly made.

(3) The hardness of the grease affects the amount which can be taken up by the leather because the harder the grease the less greasy is leather. By using a very hard grease such as parrafin wax, the leather may be absolutely filled without any feeling of greasiness. Because drum-stuffing allows the use of these hard greases and of high temperatures the amount of grease which can be absorbed is very high and it has been one of the chief factors in developing and making popular the use of the drum.

(5) Waterproofness. A leather with a high percentage of grease is more water resisting than one without. Since drum stuffing allows more grease to be absorbed more waterproof leathers can be obtained than by hand-stuffing. Drum stuffing allows the use of very water resisting materials, such as paraffin

wax and resin which could not be incorporated in dry leather by hand stuffing. The leather can be made quite waterproof yet firm and not soft and greasy whilst if the same degree of waterproofness were required by hand stuffing the leather would be both very soft and greasy.

Summarizing the Advantages of Drum Stuffing Over Hand Stuffing

(1) A greater speed.

(2) Uniformity of process in regard to both individual pieces of leather in one lot and successive lots. Uniformity of color and amount of grease. Process more under control so that amount of grease incorporated can be more easily regulated.

(3) Economy of greases. All absorbed and none wasted as with hand stuffing, also cheaper greases can be used.

(4) Heavier weights can be obtained.

(5) More waterproof leathers are possible.

The object of the application of oils and greases to leather have now been described in two parts, one in connection with the application of oil to the surface of leather during drying and the other in connection with the impregnation of the leather with grease during drum stuffing. Another object of function of the oil is that of permanency. A leather which contains grease is, other things being equal more resistent both to wear and atmospheric conditions than a leather without grease. It is difficult to determine exactly how far the increased resistance is due to or runs parallel with the fact already mentioned such as tensile strength, waterproofness, etc. But there are cases where the effect of grease in the leather is to give added life quite apart from these factors, or at any rate where these factors are not aimed for. Perhaps the best illustration is that of library books. It has been found in long experience of leather used for bookbinding purposes that leather tanned books which are handled most frequently have longer lives than similar books which are

not handled. The conclusion arrived at by the Royal Commission appointed some years ago to investigate the causes which affect the permanency or otherwise of leather used for the bindings of books, that this increased life was due to the accumulation of grease in those parts of the leather which were the most handled. The grease from the hands was removed and absorbed by the leather and helped to lubricate the fibres and prevent the rotting of the leather. This rotting effect is caused partly by exposure to light and air but mainly by gas fumes. The presence of grease in the surface of the leather helped to prevent this rotting effect.

It is evident that when leather is to be kept for a great length of time, the presence of grease may play a very important part.

For the sake of completeness it might be well to describe briefly the difference between the true oils and fats and the mineral oils. The former class are found in animals and vegetables whilst the mineral oils and waxes are obtained from the earth. The difference of origin is, however, unimportant compared with the differences of the properties between the two classes. An outline of the composition of the true oils and fats has been given. The mineral oils cannot be regarded as salts of the base glycerine, and they cannot be split up into glycerine on the one hand and fatty acids on the other. They are compounds of hydrogen and carbon and contain no oxygen. They are characterized by great resistance to chemical action, for instance, it is impossible to saponify them by means of alkali. In connection with their use upon leather, they cannot produce an oil tannage such as in chamois leather dressing, since they do not decompose in the same way and do not combine with the fibres. Their action is primarily a lubricating one and also of course, a waterproof one. Their chemical inertness renders them free from one trouble often met with in the case of vegetable and animal oils, that of spueing. Since they cannot produce an oil tannage or

combine with the fibre it is usually held necessary that some other oil should be used in conjunction with them. The mineral oil may vary from a very thin light colored low gravity oil to heavier, darker, more viscous oils through almost pasty greases such as vaseline to the various grades of paraffine wax. The thinner and lighter oils, apart from not being able to combine with the fibres, are also not very suitable for use upon leather alone because they are slightly volatile and will in time gradually disappear. The same objection cannot, however, be applied to the heavier mineral oils and of course not at all to the mineral waxes. The mineral oils are very useful to add to other greases either to make softer or harder since all consistencies of mineral oils or waxes are possible.

In many cases the oil tannage or combination with the fibres is not of first importance, for instance, where a leather is required to be filled with greases to make it waterproof. Probably such a leather has already received a coating of oil such as cod, before drying out. The use of mineral waxes for helping to make the leather waterproof is a very common one and no objection can be raised to it. When leather has to be filled with grease for the sake of waterproofing no better grease can be found than such a one as paraffine wax, since it is highly water resisting, large quantities of it can be incorporated and the leather still remain dry to the feel. Moreover, since the mineral wax is very resistant to alkalies, it will give a degree of permanency to the leather in which it is incorporated.

A case in illustration of this point is that of leather, say, for farmyard use. The alkaline character of the manure has a slow but certain disintegrating or solvent action on the grease in the leather. In time a large proportion of the grease is removed and the leather loses its "nature" and becomes weak and cracks. If the boots are frequently oiled or coated with dubbin the lost grease will be replenished and the life of the boot will be considerably lengthened. This solvent action of the manure,

etc., is most marked in the true oils and fats and is much less marked in greases of the nature of paraffin wax. Leather which contains a proportion of paraffin wax will give a larger life for this purpose than say, one which contains nothing but cod oil and tallow.

Impregnation Processes

References have already been made several times to the dipping process of incorporating grease in leather. This process differs in principle and its manipulation from either of those already described. In both the chief types of methods already mentioned, that is oiling or hand stuffing and drum stuffing, the grease is applied to wet leather. Emphasis has been laid several times on the necessity for the presence of moisture in the leather. This is to ensure proper separation of the fibres and the maintaining of a good color. The part which the moisture plays in these processes has been enlarged upon so that it may seem contradictory to describe a method in which the leather is stuffed dry and not wet. This is the main feature of the burning in or dipping process, that the grease is put into the leather whilst the latter is quite dry. The apparent contradiction between this process and what has already been said of the importance of moisture will be described later, that is after an outline of the process itself has been given. There are two general types of methods of carrying out this dry impregnation, one called "burning in," in which the dry leather is placed on a table and the hot melted grease is poured on to the leather and the other called "dipping" in which the dry leather is bodily immersed in the melted grease. The latter process is perhaps nowadays more common than the former, although both methods are used to a much greater extent than formerly.

The following is an outline of the Dipping process:

Dipping

The leather to be stuffed must usually receive rather more treatment before stuffing by this method than by say drum stuffing. For instance, the leather requires to be set out fairly well before stuffing instead of afterwards as with drum stuffing. In the dipping process the final character of the leather should be determined as far as possible before the impregnation with the grease, and the actual dipping process itself should only be relied upon to introduce the grease. In drum stuffing or hand stuffing the leather can be manipulated much more both during and after the impregnation with the grease. Put in another way, in dipping, the impregnation with the grease comes later in the stages of manufacture than in either hand stuffing or drum stuffing.

As will be apparent later, the dripping process is only suitable, or at any rate only commonly used, for leathers which are to be finished firm or heavy. The leather properly tanned and set out is dried completely. The drying is the most important of all the points to be watched in this process. So-called air drying is not enough. Something has already been said of the amount of moisture which is present in so-called dry leather and of the persistency with which moisture is held by leather. The only way to dry leather absolutely would be at a temperature of 100 degrees C for many hours. This of course is not feasible and something between this treatment and the ordinary drying in the atmosphere must be chosen. The reason why the moisture in the leather must be reduced below the limits of ordinary air drying is to avoid damaging the fibres by heat. The impregnation is made at a (comparatively) high temperature, much higher than is possible or is given in drum stuffing and much higher than damp leather will withstand without having its fibres destroyed or weakened. This is the central fact around which hang the differences between dipping and drum stuffing,

and the advantages of each process over the other. In drum stuffing the temperature is limited by the point at which we leather is destroyed by heat, whilst in dipping the limit is a similar one but on dry leather. The latter is much higher than the former. The advantage of being able to use much higher temperatures for dipping than for drum stuffing is that greases of much higher melting points and therefore harder can be used The temperatures which are safe on very dry leather (ordinary well tanned vegetable leather) may reach as high as 100 degrees C, although usually rather lower temperatures than this are used. These are much higher in drum stuffing, the average temperatures here being round about 50 degrees C (for vege table leather). Some greases therefore which melt at tempera tures higher than 50 degrees C cannot be incorporated in leathe by drum stuffing but can quite easily and safely be taken up by dipping the dry leather. Too much emphasis cannot be laid upon the importance of controlling the amount of moisture in leather to be dipped. The usual way to make certain that the leather is sufficiently dry is to take the leather after drying in the ordinary way and to hank it in a stove or hot drying room at not less than 45 degrees C. Although the drying capacity of an atmosphere depends upon the amount of moisture already in it as well as upon the temperature it will be found in practice that a room kept at 45 degrees C and used only for dry leather will dry leather sufficiently thoroughly to make dipping at 80 to 90 degrees C quite safe.

The leather therefore is first of all dried in a stove for several hours, the time depending upon the thickness of the leather, and is then immediately dipped in the melted grease The actual dipping is carried out in large vats or tanks which can be heated either by steam coils, by steam jacket or other means. The vat is filled to near the top with the grease to be used and the latter melted and brought to the requisite tempera ture. The leather is suspended on sticks by means of loops or

string or in some other convenient way and simply immersed in the melted grease. The leather will gradually if not at once sink in the grease so that the strings are taut. The tank should of course be deep enough to take the leather in an upright position without touching the bottom or slanting. Immediately the leather is immersed countless tiny bubbles of air arise. The evolution of air bubbles gradually diminishes and usually after ten minutes or so the stream of bubbles has ceased. The leather is usually left in the grease rather longer than this, that is where the maximum impregnation is required as is usually the case with this process, although where the amount of grease which it is desired to incorporate is only small, the length of time the leather is immersed may be very much reduced, even to a mere dipping in and out again. When the leather has been dipped in this way it is taken out, allowed to drip, and then usually allowed to cool by hanging up. The subsequent treatment varies with the class of leather to be dressed. For example it may merely be allowed to cool without further treatment although for most purposes it is necessary to soak it back and give it quite a series of processes.

The Burning-in Process

The other method of incorporating grease in dry leather, called the Einbrennen or Burning-in process, differs from the dipping process just outlined in that the melted grease is applied to each individual piece of leather on a table instead of by immersing the whole leather in the melted grease. The leather, which of course must be dried very thoroughly in the same way as for dipping, is placed on a table, usually grain down, and the hot melted grease is then run on to the flesh side by means of ladles and brushed in. Since the leather is very dry and also warm (the process is usually carried out in a room maintained warm so that the grease shall not set before it has had time to penetrate the leather) the grease fairly readily penetrates the

leather, particularly when it is well brushed. By this process the amount of grease given to each piece of leather can be adjusted and measured. Similarly it is possible to vary the amount given to local places, thus thick places may receive more than thin places. It is also possible even to vary the kind of grease applied to different parts of the leather. For instance, loose soft places may receive a much harder grease than stout hard places in order to produce a more uniform final piece of leather.

When this method is chosen instead of the dipping process it is usually because it enables a better color to be obtained. By the dipping process the whole of the leather from grain to flesh is impregnated, so that when such a leather is allowed to cool the surface is considerably darkened. It has already been pointed out how the presence of grease in the grain of leather produces a dark color. By drum stuffing, when the leather is moist, it is possible to maintain the surface in such a form that a film of grease does not form on the surface and so produce very much darkening effect. By dipping, on the other hand, the surface is filled with grease and the color is very considerably darkened. A good deal can be done by subsequent treatment to improve the color but by the burning-in process it is possible to maintain a better color throughout so that there is not the same need for further treatment to improve the color. In the burning-in process the grease may be applied to the flesh only and as a further precaution against the grease penetrating the grain side and producing darkening it is possible to damp the grain surface. This may be done either directly, that is, the leather itself may be damped on the grain side or the leather may be placed grain down on a layer of wet material. By having a fairly thick layer of some soft material which is maintained wet and which will yield to the inequalities of the leather, the surface of the latter can be made sufficiently moist to prevent the grease from striking through from the flesh to the grain.

The temperature of the grease may be the same as for the

dipping process, but the precsutions which must be taken with regard to the amount of moisture in the leather need not he as exact as with dipping, although it is better to err on the dry side. The reason why the danger is not so acute by this process as by dipping is that the temperature of the leather itself is lower than that of the grease and the final temperature of the impregnated leather is not as high as when the leather is dipped, because in this latter case the cooling effect produced by the leather is negligible.

The advantages of the burning-in process over the dipping process are therefore:

1. It is possible to maintain a good color more easily.
2. Weighed quantities of grease can be incorporated.
3. The grease can be altered more easily than in the dipping process. Smaller quantities of grease can be dealt with. In the dipping process the amount of grease used is considerable, and it is not as easy to modify or change its character.
4. Different parts of the same piece of leather may be impregnated with different kinds of greases.

The advantages of the dipping processes over the burning-in process are:

1. Simplicity. The temperature can be regulated and kept at the same point more easily.
2. Speed of handling. The amount of labor required is much less.

After Treatment of Dipped Leather

Whether the leather has been "dipped" or "burnt in" it is usually thought necessary to soak it back in water and to give it some of the treatment which is usually given to ordinary drum stuffed leather, such as setting out. It is thought that the soaking back in water is necessary in order to separate the grease between the fibres so that each fibre is coated with a layer of grease. If the leather be not soaked back or given no treatment after dip-

ping the tensile strength and other properties are not so good as when the leather is thoroughly softened and soaked back again and then dried out. The soaking back is usually carried out in the drum rather by suspension in water. The mechanical action of the drum helps to soften the leather, to make the water penetrate and to separate the fibres so that the finished leather resembles very closely the result that would have been obtained if it had been drum stuffed. By soaking back and setting out, the color of the leather is also very much improved. Instead of drumming in this way one plan is to immerse the leather immediately after dipping or burning-in, in a weak cold sumach liquor and to leave there for a couple of days. This allows the leather to be soaked back thoroughly and the color of the leather is improved without a great loss of weight as sometimes occurs when the leather is drummed.

Whether the leather has been soaked back by drumming or by immersion, it is set out by machine or by hand, and before or during the drying the grain is oiled very lightly and sometimes the grain is moistened several times with water. It will be evident, therefore, from the brief description of the after treatment given to dipped leather, that the process is really not an exception to what has been said of the necessity of moisture in the leather in stuffing, because in this case, although the grease is put into the dry leather, it is necessary to wet back the leather in order to produce the best results.

Advantages of Dipping or Burning Drum Stuffing

The differences between the conditions which obtain in drum stuffing and in dipping have already been discussed and the advantages of one process over the other are dependent upon these different conditions.

1. Harder and More Greases Can be Incorporated

In dipping, the impregnation is carried out upon the dry leather; in drum stuffing upon the damp leather. Dry leather

will withstand much higher temperatures than wet leather. The harder the gresse the higher the melting point. Taking these facts together, it is possible to use much harder greases in dipping than in drum stuffing. This is an advantage in certain cases, where for instance a leather is required very waterproof but must not feel or look greasy. By the use of very high melting point waxes the resultant leather may contain large proportions of very waterproof greases and yet maintain both a light color and a non-greasy feel and appearance. For similar reasons it is possible to incorporate larger quantities of grease by dipping than by drum stuffing. In the former process the leather is filled with grease to the limit whilst in the latter process the presence of moisture, which must afterwards be removed, prevents the spaces between the fibres from being completely filled with gresse.

2. Simplicity

By the dipping process there is no trouble about sammying the leather or getting it into exactly the right condition for stuffing. In drum stuffing the leather must be carefully dried and all parts must be uniformly moist to obtain uniform absorption of grease. In dipping the grease is uniformly absorbed without any effort and there is no trouble with certain places taking more or less than their share of grease as is often the case in drum stuffing. The amount of space required for the dipping process is not as great as for drum stuffing, and there is no power required except the steam for heating the grease.

The degree of skill required is also not so great with dipping. The temperature is maintained constant, and this is much easier than having a fluctuating temperature as in drum stuffing, where very often the temperature is only a few degrees from the danger point and in which it is more difficult to control the temperature.

3. Uniformity

Since the leather is always completely dried out for dipping the amount of grease taken up is uniform not only throughout one pack of goods but also with successive packs. In drum stuffing the extent of drying fluctuates very considerably, being dependent upon the state of the atmosphere. The personal equation also enters very largely into the operation of drying before stuffing. Reliance has to be placed upon such elusive things as appearance and feel. Uniformity of dryness is therefore difficult to obtain, and it influences the leather in two ways. In the first place, if the leather is too dry the grease is absorbed too readily, and the color and tensile strength are depreciated. In the second place, the weight of the grease to be given is based upon the weight of sammed leather so that the wetter the leather the more grease (relative to the weight of the dry leather) is given.

In dipping, all these variations are done away with and the amount and nature of the grease absorbed are always uniform.

Oil Tannage

An article on the application of oils to leather would scarcely be complete without a description of the oil tannages or the methods of producing leather from pelt with oil alone as the tanning agent, although strictly speaking it is not a case of the application of oil to leather. Some reference has already been made at the beginning of the article to the early methods of tanning and it was described how the methods of impregnating skins with oil and fat and then subjecting them to a squeezing action was perhaps one of the earliest methods of converting the putrescible skin into something permanent, that is, into leather. It is a far cry from the crude methods and products of those early times to the modern methods of making chamois leather which is the best example of a purely oil tannage.

When discussing the differences between vegetable and animal or fish oils on the one hand and mineral oils on the other

it was pointed out that the latter are very stable materials and resist both internal changes and the action of chemicals upon them. The true oils and fats, that is, the common vegetable, animal and fish oils, are easily split up by external agents and some of them also undergo internal changes especially in contact with air. It is only these latter oils which can successfully be used in producing an oil tannage and for producing chamois leather the use is almost confined to one of three oils, cod, seal or whale. An outline of the process of chamois leather making is as follows:

The flesh splits from sheepskins are used. The sheepskins are split when the wool has been removed and usually after the skins have been limed. The object of the liming is to swell the skins so that they will stand up to the splitting machine. From the splitting machine they are taken either to be limed still further or to be drenched.

The oil is applied to each piece and the heavily oiled fleshes are placed in the faller stocks which consist of a box-like arrangement in which a huge hammer works backwards and forwards. The action of the stocks presses the pieces whilst the position of the latter are continually changed. The somewhat violent action of the hammer causes the oil to be driven into the interior of the skins. More oil may be added until the skins have taken up as much as is possible. The oil impregnated skins are then hung up in warm rooms. A large surface of oil is thus exposed to the air which at the relatively high temperature causes the oil to be oxidized. After a certain length of time the skins are taken down and packed in wooden tubs or boxes. The oxidation and other changes in the oil are continued and accentuated in the confined space of the tubs and the skins become hot. When they have become sufficiently hot they are removed and either hung up again or further oiled in the faller stocks and the above process repeated.

By the repeated oiling and heating, the pelt is converted

into leather. The leather is yellow, extremely flexible and soft and is in fact ordinary chamois or wash leather.

There is always a large excess of oil and it is this excess of oil which has of course, undergone change and oxidation, which is removed by different methods and which constitute sod oil and degras. The difference between sod oil and degras depends on the methods adopted for the removal of the excess oil.

In the English way the oxidation is allowed to take place much more rapidly, so that it is also much more intense. The skins, after being impregnated with the cod liver oil by stocking, are hung up in warm rooms in which oxidation commences. They are then either packed in tubs or laid in piles. The oxidation here continues and the temperature may be so great that it becomes dangerous; constant supervision is required. This process may be repeated one or more times. When the oxidation is considered to have proceeded far enough the residual oil is removed by scouring the skins with alkili. The aqueous liquor containing the oil is then treated with acid, by which the oil is partially separated from the water. This product constitutes sod oil. It is more viscous and usually much darker than that obtained in the French method.

In the French method the oxidation is only allowed to proceed slowly, and the temperature is not allowed to rise so high. In addition to this, whale and seal oils are used as well as cod liver oil. The resulting oil is more liquid than sod oil and is removed by pressing. As obtained in this way it constitutes moellon. The oil may be removed by a series of pressings, the first of which of course, yields the best product. Procter states that this moellon is never sold in this form but is mixed with further quantities of fish oils, tallows and sometimes wool fat. The mixtures obtained in this way constitute the ordinary commercial degras. A further quantity is removed from the skins after pressing in a similar manner to the English, that is

by scouring with alkali and further treatment with acid. This yields a poorer quality of degras. As already mentioned the amount of oil obtained in this way as a by-product in the manufacture of chamois leather, is not sufficient to meet the demand, so that nowadays some manufacturers make the manufacture of sod oil the main part of the process. To achieve this they use the skins repeatedly for the production of sod oil, that is, after the removal of the sod oil in the way described, the skins are further impregnated with cod liver oil and the usual processes repeated. More recently methods have been devised for the production of sod oil without recourse to the oxidation of cod liver oil by means of skins. In these processes the oils are oxidized directly.

The above is an outline of the use of oils for producing chamois leather.

Other examples of oil tannages are Buff leather, Japanese White leather, Napa leather. The principles are the same in each case, the differences being due to different classes of skins and to the variation in details. Thus Buff leather was made from antelope or deer skins. The grain of the skin was buffed or "frized" off after lining. The oil tannage was carried out in a similar manner to that described.

Japanned Leather

The production of japanned, patent or enamelled leather depends upon the application of certain oils to leather. Perhaps no leather has been surrounded by so much secrecy as japanned leather. The making of the varnishes, the preparation of the leather and all the paraphernalia connected with the process have been regarded as secrets to be jealously kept. Stories are told of craftsmen of this leather maintaining their recipes and secrets until their deathbed and then only telling their own sons with an injunction that they shall maintain the same secrecy. This was in the day when leather making was carried out in a

small way, in a back yard as it were. Nowadays when the tendency is for leather making to be carried out on a large scale the same secrecy is not possible. Moreover, the advent and the application of science to the leather industries has unlocked many of the secret doors and has led to the possibility of producing similar leathers by quite different methods. The main difficulty lay in the preparation of the varnishes and the formulae for these were very complicated. As in the case with many of these old fashioned recipes some of the constituents seem to be useless, but probably each of them had been found to fulfil some useful purpose, in some connection if not for the one immediately concerned, so that it is not always wise to scoff at these complicated recipes. Modern chemistry has shown the function of many of these ingredients and has been the means of suggesting simpler and more rapid methods of producting the same effects in addition to pointing the way to quite different methods of producing patent leather.

In all the processes of making japanned leather, leaving out of account, for the moment, the newer methods of soluble cotton varnishes, linseed oil was the main material. Linseed oil is perhaps the best example of a drying oil. If a film of linseed oil be formed on a glass slide and left exposed to the air, it slowly becomes more viscous until in time it sets to a dry elastic film. This process of natural drying is of course much too slow and uncertain for industrial purposes and use is therefore made of materials which accelerate the drying. In the making of patent leather, the basic principle is the production on the surface of the leather of a highly glazed film of dried linseed oil which is both flexible and tough. The drying of the oil is brought about by the absorption of oxygen. Under natural conditions this absorption is slow, but it can be accelerated by the addition of certain substances which are called "driers" or "siccatives." These driers are sometimes bodies which behave as oxidizing

agents and contain within themselves the oxygen necessary to produce the drying of the oil. More often these substances behave merely as conveyors of oxygen from the air, that is they behave as catalysis. They themselves are not changed by the process and they increase the rate at which the oil absorbs the oxygen from the air.

Such materials are metallic salts and compounds such as litharge, Prussian blue, manganese borate, manganese peroxide, raw umber, lead acetate.

Preparation of the Varnish

Boiled linseed oil is used as the base for the preparation of the varnish. If the ordinary, that ie, raw linseed oil be taken it must first of all be boiled. It is better to start with raw linseed oil and to add to it during the boiling one or more of the materials already mentioned rather than to start with linseed oil which has been boiled with no additions.

The driers or siccatives must be in a very finely ground condition and must also be quite dry. It is obvious that any large solid particles would prevent the final surface from being perfectly smooth and glassy. There are many ways of making up the varnish but the following may be taken as a type. Raw linseed oil is taken and to it added 2 to 3 ounces of litharge, in a very finely ground state, to each gallon of oil. The mixture is then brought to a temperature of about 250 to 260 degrees C. Care must be taken that the frothing does not become excessive. If the temperature be raised too high the reaction is too violent and the liquid will froth over. This boiling was usually carried out in open pans over open fires and there was therefore always a great risk of fire so that it was usual to perform the boiling out of doors. The boiling is continued for six or seven hours. The oil becomes gradually thicker and more viscous. An experienced man judges by the appearance of the varnish when the boiling has been sufficient. Thus if a drop of the varnish

be taken out and poured on to a smooth surface and the finger dipped into it and then removed, threads of several inches will be obtained if the boiling has been long enough.

Along with the drying agents other substances are added to produce the requisite color. These substances are pigment colors, as of course aniline dyestuffs are not suitable. They may also act as driers themselves. Most patent leather is made black and for this purpose the pigments which are used are Prussian blue, vegetable black (finely divided carbon). For colored varnishes many of the common pigments such as chrome yellow may be used.

These materials are added to the linseed oil during the boiling. When the mixture answers the test it is usual to pour it through a sieve made of fine mesh copper wire gauze to get rid of coarse particles.

Preparation of the Leather

Before the varnish or enamel is applied to the leather, the latter must be suitably prepared to receive it. Certain precautions must be taken. Thus the leather must be quite dry and also free from grease. The presence of grease in the leather will prevent the varnish from adhering properly to the leather, causing the former to peel or "fly." For this reason it is advisable when the necessary plant is available, to remove any grease which may be present by means of a special degreasing plant. When this method is not feasible it is wise to take precautions in all the processes through which the leather or skins pass, to remove the grease so far as possible. Thus in the beamhouse processes it is well to give extra liming to saponify and remove the grease. The scudding should be carried out very thoroughly for the same reason. Similarly in the processes of finishing the leather no stuffing or currying is feasible. The leather must be made soft without grease, either by using mellow tanning materials or other means. If a special degreasing plant be available the pro-

cess is much simplified because the leather can then be made soft in the usual way by means of oil or grease which can be removed. (If a leather be curried or oiled and the grease then removed by a grease solvent as in a degreasing plant, the product will be much softer than if it had been finished without oil or grease. This point has already been discussed, when it was pointed out that the softening qualities of an oil in leather are not due so much to the presence of the oil itself as to the action of the oil on the fibre as the leather dries. Oil applied to a dried leather has nothing like the same effect on the softness and suppleness of the leather as when applied to the wet leather. If therefore the oil be removed from a curried leather the latter will still remain soft and supple.) This plan of degreasing is also of advantage for making japanned leather because it enables the manufacturer to buy his leather from outside sources. He need not be afraid of the presence of grease because he can degrease all his leather and so make certain of the absence of grease. When no degreasing plant is available it is sometimes wise to remove the grease from the surface by means of benzine or petrol. Linseed oil may be used for oiling the leather and this will not cause the leather to lose its affinity for the varnish.

Having made certain that the leather contains no grease, the surface of the leather must be prepared to receive the varnish. For this purpose one of the first essentials is that the leather be set out very thoroughly to remove all stretch. When a split leather is to be enameled the surface must be shaved very level, even and smooth. The surface may also be stoned or pumiced. The leather before being enameled is thoroughly dried and also often tacked or nailed on to frames. The enamelled surface is never produced by one application of the varnish. The first coat is usually the heaviest and thickest. This is technically known as the daub. The leather having been set out and dried is given the first coat and then transferred to the

stove with little application of heat. When dry the surface is made smooth by rubbing with pumice stone. A second coat is then applied, made thinner and given more sparingly. The second drying is then given at a rather higher temperature in the stove. The surface is again smoothed with pumice stone and the third and final coat of varnish applied. For this purpose the room in which the operation is carried out must be as free from dust as possible. When the last coat has been applied the leather is dried in a very hot stove and finally in the open air until no longer sticky when pressed with the finger.

Recently the above process of producing enamelled leather has been largely replaced by the newer nitrocellulose varnishes, used either alone or in conjunction with linseed oil varnishes.

This is quite a separate branch and hardly falls within the scope of an article on the application of oils.

Hydrogenated or Hardened Oils

Many oils which are liquid in the natural condition can be converted into solid substances by a chemical treatment called hydrogenation. The fatty acid from olive oil is called oleic acid and is liquid, stearic acid is a hard wax like substance and is the main constituent of currier's stearine. Oelic acid differs from stearic acid in a chemical sense in a very simple way. The molecule of stearic acid is identical with that of oleic acid but plus two atoms of hydrogen. It has long been the aim of chemists to find in an easy and commercial way of adding these two atoms of hydrogen to the molecule of oleic acid, that is of converting oleic acid into stearic acid.

Recent methods have been devised and enlarged to a commercial scale, of making oleic acid and kindred liquid oils combine with hydrogen to form stearic acid or other solid greases. The basis of the method is that hydrogen is passed into the oil in contact with some catalytic agent such as certain nickel compounds which enable the oil to take up the hydrogen but which

itself if not a constituent of the final product, so that it can be used again. Thus by one process the oil is thoroughly mixed with a small quantity of the catalyst, for instance, with one per cent of nickel oxide, and hydrogen gas at a temperature of 150 degrees C to 200 degrees C is passed through the mixture. By passing the hydrogen for a long time the final product becomes very hard and it is possible to obtain all stages of hardiness.

This process is an outcome of the discovery in 1901 by Sabatier and Senderens that organic substances can be reduced or made to combine with hydrogen in the presence of finely divided nickel. By this process they were able to build up a large number of other substances. Search for a practical application of this principle resulted in many patents of which the most famous was that of Normann, who applied the process to the reduction of unsaturated oils. Norman's patent of 1904 was the main one, and many others since then have only differed from it in detail.

The process for the application of this principle of addition of hydrogen to oils by means of a catalyst, is now very widely applied and there are very many and large works for converting liquid or pasty oils into solid fats. The method of adding hydrogen to organic substances by means of a catalyst may be applied to many other substances besides oils as Sabatier and Senderens showed twenty years ago, but the application of the process to oils is easily the most important and the largest of all used.

It may be asked why is it of advantage to convert a liquid oil into a solid substance and what benefit does a solid fat present over an oil. Perhaps this will be more apparent when describing the uses of the hydrogenated products, but as a general statement it may be taken that a solid fat is more valuable than an oil, and also that the harder the fat the more valuable it is. Thus as an illustration the cases of stearine or paraffin wax may

be taken. These are usually sold on the melting point, and the higher the melting point (when dealing with the same substance). Thus the difference in price between a soft parafin wax of a melting point of 110 deg. F. and a hard one of 140 deg. F melting point is perhaps more than 50 per cent. If, therefore a soft grease can be converted into a hard one its value is increased. As will be seen later the hardened product may be used for purposes for which the liquid or softer materials is quite unsuitable.

Perhaps the term catalyst which has been used several times should be explained. There are many reactions in chemistry and in many commercial processes (in the conversion of pelt with leather very many cases occur) in which catalytic action o catalysts plays a part. A catalyst is a substance which allows a certain reaction to proceed or which rapidly accelerates a re action between other substances, but which itself is not a constituent of the final products of the action. They have been likened to the lubricant in mechanics which allows, for instance a shafting to revolve without friction, but which remains unaltered by the process.

Thus in the case of hydrogenation of oils by means of the catalyst, finely divided nickel, the amount of nickel is the same after the process as before. If hydrogen were passed direct into the oil without the nickel, little or no change would occur but in the presence of the finely divided nickel the hydrogen rapidly combines with the oil and hardens it. The nickel remains apparently unaltered at the end. It behaves as the lubricant does in a shafting or bearing. The amount of the catalyst required to produce the change is a very small fraction of the amount of the material acted upon. Moreover, the catalyst can be used again and again so that it is possible for a very small quantity of the catalyst to convert an almost unlimited quantity of the substance acted upon. On the manufacturing scale the catalyst is very rarely used over and over again without some

treatment. It is found that it gradually loses its efficiency, perhaps through being soiled or fouled by extraneous substances, and it is usual to treat the catalyst after a certain length of usage to make it efficient for a further lot of material. Several theories have been advanced to explain this phenomenon which are rather beyond the scope of this article, but one of the best known is that the catalyst does not remain unchanged but that it alternately combines with one or other of the reacting substances and splits off again, so that at the end it remains in the same condition as at the beginning. According to the lubricant theory held by Ostwald, the reaction is only accelerated by the catalytic agent and the reaction must be actually in progress before the catalytic agent can act. In very many cases this is no doubt sufficient, that is, in many cases the catalytic agent behaves as a stimulant, but there are several cases where the reaction can be started by the catalyst and there are cases even where it may actually retard a reaction. A more important point is that although the presence of the catalyst may alter the speed of a chemical reaction, yet the condition of final equilibrium is not affected. This has been proved in the case of the manufacture of sulphuric acid by the contact process, which is perhaps the largest commercial application of a catalyptic process. In this process, sulphur dioxide gas and air are passed through tubes containing platinized asbestos, that is, asbestos which has been so treated with salts of platinum that it presents a very big surface of finely divided metallic platinum. The presence of the platinum causes the sulphur dioxide and the oxygen of the air to combine to give sulphur trioxide or sulphuric acid. Without the platinum the two substances would not combine. The action of the platinum may be somewhat as follows: The platinized asbestos has tremendous affinity for gases and will absorb or occlude very many times its own volume of gas. Thus the concentration of the molecules of the gas at the surface of the platinum is very many times the concentration of the substance in the free gaseous state. This

will result in very many more collisions between the molecules of the reacting substances at the surface of the platinum than in the free gaseous state. In other words the rate of reaction between the two substances is considerably multiplied.

Although the subject of catalysis and the behavior of hydrogen in contact with finely divided platinum or nickel has been the source of very much theorizing, yet very little is definitely known of what happens.

In the hydrogenation of oils a similar thing occurs; the oil is intimately mixed with the catalytic agent, usually either finely divided nickel or nickel oxide. The hydrogen is passed through or over the mixture and is absorbed very rapidly. After removing the catalyst for use upon a further quantity of oil, the hardened oil may be further treated by a process of purification.

The use of the hydrogenation process has perhaps been the most extended in the candle and the edible fats industries, the latter having of course received a wonderful impetus during the war due to the shortage of butter and the other natural edible fats. Other industries also have benefited from the use of hydrogenated products.

In the candle industry, liquid oils themselves are of course useless, but by the hydrogenation processes many oils and fats which would otherwise be unsuitable are made very valuable. Similarly in the soap industry.

With regard to edible oils and fats, oils have very limited uses whilst a solid fat can be made to replace butter, lard and the various edible fats used for example for culinary purposes such as fish frying.

During the war many solid fats have disappeared from the market altogether or have become scarce and prohibitive in price. Thus to take a case of most interest to the leather trade, that of tallow:—very large quantities of tallow are used in hand stuffing and also in drum stuffing but the price during the war has risen 200 to 300 per cent. In England therefore substitutes have been

sought for tallow in the leather industry, and one of the most important changes which have taken place in the application of oils and fats to leather during the war has been the substitution of hydrogenated fats for the usual fats such as tallow and stearine. Of the oils which have been found most suitable for hardening by this process to replace tallow and other stuffing greases, seal and whale oil are perhaps the most important. For edible purposes, oils of vegetable origin such as cotton seed oil have been the most valuable for hydrogenation.

The hydrogenated product differs from the original oil not only in being harder, (which constitutes its chief value) but in other ways. The final product is much lighter in color than the original oil, many of the hydrogenated substances being quite white like good tallow. From the leather dresser's point of view this is a great advantage, for light colored greases have always been more in favor than darker ones. Two greases which are alike in all properties (such as hardness and consistence) other than that of color, may differ considerably in price. This difference in value according to color is probably largely unnecessary in many cases for leather dressing purposes, and has probably arisen from the very doubtful and sometimes quite erroneous assumption that a dark oil or grease must necessarily produce a corresponding increase in the color of the leather. With the present outlook that a light colored grease is more valuable than a dark one, then the process of hydrogenation will raise the value.

With many oils the hydrogenation process takes away any disagreeable odor. For edible fats, the vegetable oils such as cotton seed are chosen for hardening, although hardened fish oils may be so purified and de-odorized as to be quite suitable for food purposes.

Another use for hydrogenated oils in the leather trade is in connection with japanned leather. In Germany, it is stated that raw linseed oil for patent leather has been largely replaced by hydrogenated linseed oil. Leather fat liquored with a hydro-

genated linseed oil may be made to contain up to 9 per cent and will still allow the japan to be put on top of it.

Those tanners who are usually afraid of chemicals may look askance at a chemically treated oil and may think that it is not as good as a natural oil or fat. The same prejudice was felt against sulphonated oils. In the latter cases ill-informed people would say, "How can an oil containing sulphuric acid be safe?" That prejudice and of course ignorance is still perhaps existent, but there is even less excuse for it in connection with hydrogenated oils, for the chemical treatment they receive only alters them in physical properties and they are incapable of exercising any chemical function which would be harmful either as a food or as a leather dressing material.

Precautions Which May be Taken to Ensure a Good Color

Before passing to the remaining method of incorporating oil or grease in leather, that is, the process called fat liquoring, it may be well to discuss some of the factors which influence the color of the leather. When it has been stuffed either by hand, by drum or by dipping.

It is unfortunate that good color should be taken as a criterion of quality or should be in such demand. In many cases, the color itself is quite unimportant and is no guarantee at all of the essential qualities of a leather. For instance in belting leather the primary qualities should be tensile strength, freedom from stretch and slip, and permanency. The color itself is of no moment at all and is not even a guide as to the other qualities. In fact in many cases a good color is obtained at the expense of the other essential properties, that is, by the special means which are taken to obtain a good color some of the other good qualities are impaired. The question is on a par with the color of sole leather, which is always desired light and in the production of which the wearing qualities of the leather may be impaired. In

this latter case the question is rendered ever more stupid because the grain of the leather is either buffed off or blackened before the boot is sold. Short of being able to educate the public and through them the manufacturers to a better understanding of the meaning of the color of leather, the tanner and the leather dresser are bound to supply what is demanded.

The influence of the amount of moisture in the leather has already been fully described as well as what causes the darkening effect when oil or grease is present as a film on the surface of the leather. The color of the leather itself apart from the presence of grease, that is, the color the tanned leather would possess if dried out as carefully as can be, has of course a very great influence. If the natural color of the leather itself be dark it is impossible to expect a light color when stuffed. The nature of the tannage plays a great part. It can hardly be expected for instance that a leather tanned with mangrove can yield as light a color as one tanned with gambier. Where a good color is desired therefore in stuffed leathers, the preliminary tannage must be taken into account and light colored tannages should be chosen where possible. If the crust leather be dark then something can be done to lighten the color before the leather is stuffed. (The darkness of the dried out crust leather may, however, be deceptive. It may not be due to the actual color of the tanned grain but may be caused by surplus tan in the grain, which would possibly be quite removed in the treatment usually given before stuffing.) If, however, the leather is actually a dark color, something may be done to improve the color by sumaching. This was at one time an almost universal process to apply to all leathers before being stuffed. The leather is soaked back in water and then either drummed or paddled in a warm, fresh infusion of sumach, to which a little gambier is also sometimes added. This produces a marked improvement of the color, which seems to be due to the sumach stripping some of the

darker colored tan from the surface and replacing it with its own lighter colored tan.

Instead of using a drum or a paddle a vat may be used in which the goods are left immersed for several hours or even days. This vat is strengthened up with sumach occasionally and may be warmed up before each lot of goods is immersed.

As dressers of curried leather very often buy many different classes of leather in the crust form, if no preliminary treatment were given, the color of the final leathers would vary very much according to the original tannage. Besides giving a sumach bath as just described many dressers scour the tanned goods. This of course precedes the sumaching. The goods are soaked back and then scoured by machine with a supply of water. This removes the bloom and surface tan and helps to produce more uniform results. The leather is then sumached. Of course by both these processes a proportion of the tan is removed and weight is lost so that the two processes are only given on best class goods or where weight is not the only consideration.

A leather which has become stained during the processes of tanning will of course still show the stains in the stuffed leather. For instance a leather which has been lime blasted or which has not had the lime properly removed before tanning will still show the stained effects after stuffing. With leathers which are badly stained and which are not made sufficiently even in color by scouring and sumaching it is often the practice to "clear" them by means of bleaching agents such as a weak solution of sulphuric acid. This practice is usually condemned on the grounds that the permanency of the leather may be very much impaired.

The extent to which the leather is tanned also plays an important part. An undertanned leather takes the grease badly and will produce a poorer color when stuffed than a well tanned leather. Similarly an over tanned leather, one with an excess of free tanning matter, will produce an inferior color. By

scouring and sumaching, as just described, both these defects are remedied to some extent, the scouring will reduce the over-tanned effect and the sumaching will make good the deficiency in tanning so that more or less uniform conditions with regard to extent of tannage are obtained.

Next to the original color of the leather the amount of moisture in the leather plays the most important part in the production of a good color and this has already been fully discussed.

Amount and Nature of Grease Used

It goes without saying that the amount of grease in the leather has a very great influence on the color. The more grease that is incorporated the more difficult it is to obtain a light color.

The nature of the grease also has an important bearing on the color. The softer or more oily the grease the less of it can be taken up by the leather without becoming dark or oily on the surface. It is this which has made the use of hard greases such as paraffin wax and stearine so popular and which has brought the methods of drum stuffing and dipping to such prominence, since by the use of these methods and greases much larger quantities of grease can be incorporated without producing dark oily effects on the grain. The harder the grease and the lower the proportion of oil in it, the more can be incorporated and still maintain a good color. Apart, however, from the question of hardness, the character of the grease has an influence on the ease of penetration and upon the color of the final leather. Thus a grease which will emulsify with water will penetrate the fibres much more readily than a non-emulsifiable one.

Influence of Degras

It is for this reason that many curriers always prefer to have a proportion of sod oil or degras in stuffing mixtures.

These materials, which are products of the manufacture of chamois leather in which cod oil is allowed to become oxidised as already outlined, are emulsifiable with water. In fact as they usually come on to the market they already contain a fair proportion of water, 20 per cent being quite common. They confer this property of mixing freely with water upon other greases to which they may be added. They are therefore very valuable adjuncts to stuffing mixtures. The property of mixing with water is a valuable one from the point of view of penetration. Since the leather is always stuffed wet (with the exception of dipping—in which case degras and sod oil are not used) the presence of a proportion of either of these two greases helps the stuffing mixture as a whole to penetrate the leather more readily. This is caused by the lower resistence of the wet fibre against the penetration of grease which is more or less miscible with water. It is akin to the penetration of oils by the process of fat liquoring which will be dealt with later. Not only is the color of the leather improved by the better penetration caused by the presence of an emulsifiable grease such as degras, but the leather itself is improved in quality. The better penetration of the fibres produces a mellower and fuller feel or what is sometimes called a well nourished leather.

Emulsifiable Greases

Recently there have been placed on the market several solid greases which are emulsifiable with water. Something will be said later about the process of sulphonating or sulphating oils which is now largely practiced and which will render an oil which is ordinarily quite non-mixable with water, capable of being emulsified quite easily. For instance, if a few drops of say castor oil or cod oil be shaken up with water, the two do not mix or emulsify. The oil may be broken up into smaller globules but they will fairly quickly come together again and form a layer on the surface of the water. By the process of

sulphating either of these two oils, the remaining products are very similar in appearance to oils, they feel oily and produce the same effects as oils. When used on leather they lubricate the fibres and produce the same softening effects as ordinary castor or cod oils. They differ, however, very materially in the way in which they behave towards water. If a few drops of sulphated oil be shaken with water, instead of coming together again and rising to the surface the oil is separated into countless small globules, so small that they are beyond the limits of unaided vision, and the appearance of the mixture is milky. The globules are so small that they do not answer the forces of gravity but they remain in suspension in the liquid for a great length of time. This is called an emulsion. (Ordinary milk is an emulsion of cream with water.) Oil in this extremely finely divided condition will readily penetrate wet leather. Such oils have been known for a long time but the last few years have seen a similar process applied to solid greases. Nowadays it is possible to obtain greases as hard as paraffin wax which are emulsifiable with water. Of course, the grease in the solid form is not emulsifiable but when the solid grease is melted and the liquid grease then shaken with water and emulsion is obtained. On cooling such an emulsion the grease may not separate out but the tiny globules will be solid. If such greases are used in drum stuffing, they will, of course, first be melted and their properties of emulsification will come into play. They will penetrate wet leather much more readily and they will separate the fibres and produce a better filled and nourished leather than greases which are not emulsifiable. The effect on the color will also be a good one. Such greases need not necessarily be used alone to allow of their emulsifiable properties being used, they have the property of conveying this property to other greases with which they are mixed. It is, therefore, quite com-

mon to use only a proportion of these emulsifiable waxes or greases in the drum stuffing mixtures.

The use of such materials enables good color to be obtained more easily.

Instead of adding one of the solid emulsifiable greases to the stuffing mixture many leather dressers use the sulphated oils just mentioned. Where particular firmness is desired the solid may be used but in many cases oil is a constituent of the drum stuffing mixture. By one of these the oil ordinarily used may be replaced by one of these sulphated or soluble oils which will render the whole of the stuffing mixture in a condition to be more easily absorbed by the leather.

Removal of Grease From the Surface

Since one of the commonest causes of dark color in curried leather is the presence of oil on the surface it naturally follows that one of the best means of improving the color of stuffed leather is to remove the grease from the surface. This is not as easy as might appear. An ordinary degreasing apparatus in which the whole leather is immersed in a grease solvent is not suitable because it would have to remove far more grease than would be feasible, in order to improve the color. An ordinary degreasing plant would not remove the grease only from the surface and that is what is required. Certain aqueous degreasing agents are, however, sometimes sold. These are really organic grease solvents which are emulsifiable with water. A small proportion of these materials along with water is placed in a drum with the leather it is desired to degrease. It is claimed that, by drumming, some of the surface grease is removed and the color is improved.

There are also methods available involving the use of alkalies which will remove the grease from the surface.

Methods of improving the color which involve actual bleach-

ing processes such as the alternate use of sulphuric or oxalic acid and soda need not be described here.

In connection with this question of removal of grease it might be pointed out that even if the whole of the grease be removed by a proper degreasing plant, some of the effects of the grease are not removed. In other words, a leather which has been stuffed or oiled and then had the whole of the grease or oil removed is not the same as a leather which has never been oiled or stuffed. The separation of the fibres will not have been interfered with by the removal of the grease. The tensile strength, although lowered by the degreasing operation will still be higher than a leather which has never been stuffed. The effect on softness and pliability will also remain after degreasing, in fact the leather may be softer after degreasing than before, particularly if the grease used in stuffing has been a hard one. The effect on the color may also be beneficial, for instance, if the leather be dark in places due to surface grease. a degreasing process will remove it and make the color uniform. For certain classes of goods, therefore, degreasing may usefully be employed, for instance, in some cases the presence of grease itself is not desired and yet a soft flexible light colored leather is wanted. One way of producing this is first to impregnate the leather in the usual way and then remove the grease.

Fat Liquoring

A discussion of this process will be rendered much easier if what has already been said about the application of oil to leather is borne in mind.

The process of fat liquoring is merely a special form of applying oil to leather. In the processes already described the oil or grease is applied in its natural form, and any variations which are possible are made in the condition of the leather, temperature of the greases, etc.

By fat liquoring, the oil is presented to the leather in a special form called an emulsion. Something of the nature of an emulsion has already been described. An oil emulsion is merely a mixture of oil and water in such a form that the oil is so finely divided that it does not separate from the water but remains suspended. Milk is a typical emulsion of butter fat in water. The particles of oil although lighter than water, do not answer the forces of gravity but remain in suspension in the liquor. The better the emulsion the more slowly does the oil separate from the water. The cream from milk will rise to the surface in several hours but other emulsions may remain permanent for days or even months. An emulsion will appear homogenous to the eye but under the microscope small spherical globules of oil can be seen.

Most of the ordinary oils will not emulsify with water by simple admixture. Means must be taken to cause the oil to be split up into very fine particles. If a few drops of one of the ordinary oils be poured into a test tube along with ordinary water and vigorously shaken, the oil will be broken up into many tiny globules but on standing for a few moments the drops of oil gradually rise to the surface and join together to form a continuous layer. Even the moment after agitation the liquid is not milky in appearance. If instead of pouring the oil into water, it be poured into a hot solution of soap and then shaken, the liquid will become milky and the oil particles will be so finely divided that they either will not rise to the surface and the liquid will remain milky, or they will rise to the surface very much more sowly than without soap. Such a mixture of oil, soap and water is an emulsion and is called a fat liquor. Until recently the use of oil and soap was almost the only means adopted for making fat liquors or emulsions to be absorbed by leather, but it will be shown later that other means are available for producing stable emulsions. When a fat liquo

is spoken of an emulsion of oil and soap is usually thought of so that in what follows, such a mixture must be understood although most of what is true for an oil and soap emulsion is also true for the other types of emulsion just mentioned.

An emulsion is not necessarily one of oil in water, many other substances may be emulsified, in fact it is possible to emulsify a solid.

Professor Meunier has carried out researches on the formation of emulsions and of the causes which lead to stability of the opposite and the writer is indebted to him for some of the following points dealing with the theory of emulsions. Certain factors are common to all emulsions whether produced by oils or gummy substances or even solids, but in the following considerations special emphasis is laid on the type of emulsions used in fat liquoring leather, that is, emulsions of oil in water produced by means of alkali, soap, or other agents. In fat liquoring, the aim is to produce a permanent or stable emulsion, and to avoid conditions which would break up the emulsion, whilst in other industries, the formation of emulsions is to be avoided. An emulsion is called stable or permanent when, if it be left at rest, the emulsified particles have no tendency to coalesce, agglomerate or finally to separate from the intergranulary medium in the form of a homogenous mass. Amongst the most remarkably stable emulsions one may cite the case of the oil emulsions of egg yolk and of milk. It is possible artificially to produce emulsions which maintain their stability for months or even years such as those obtained by prolonged agitation of wool grease with alkaline water or the emulsions of lubricating oils that are sometimes produced in the condensed water from steam engines.

Sometimes it happens that a separation occurs which may be mistaken for a breaking of the emulsion. Thus when the intergranular substance (the medium in which the substance is

emulsified), is liquid and is in great excess of the emulsified substance, the emulsion itself may separate from the excess of the liquid, either by rising to the surface or falling to the bottom depending upon whether the emulsified substance is lighter or heavier than the liquid. The emulsion is not necessarily broken and the emulsified globules may still remain separate. What happens is that the emulsified particles remain separate but they carry with them part of the emulsion medium, leaving the remainder of the latter free from the emulsified substance. An example of this is milk in which the emulsion of the fat rises to the surface. The fat globules do not coalesce and the cream on the surface is still an emulsion. Attention has been drawn to this point because sometimes commercial fat liquors separate in this way and they are then regarded as unsatisfactory. An emulsion which behaves in this manner may be perfectly satisfactory in use and should not be confused with one in which the oil globules coalesce and rise to the surface as a transparent liquid. The latter case is one of true separation of the oil from the other liquid whilst the former is merely a separation of the emulsion itself from an excess of the liquid.

True emulsions of oil in water are characterized by being more viscous than the oil from which they are made.

The Size of the Particles in Stable Emulsions

Evidently one of the most important factors in connection with emulsions from the point of view both of its influence on the stability of the emulsion and of the behavior of the emulsion in practice (e. g. in fat liquoring, the case of penetration) is the size of the emulsified particles. For emulsions of solid particles a centrifugal method may be used to determine the size. A microscopic method involving an actual counting of the number of particles in a given volume of the emulsion may also be used. In the case of liquid substances the ultra filters of Bechold may be used to determine the size of the particles. These filters

are made by impregnating a filter paper with colloidal solution of collodion in acetic acid. By varying the strength of the solution of the collodion the pores of the filter papers are made of definite size. By passing the emulsion through various of these filters until one is found which is the limit which allows the particles of the emulsion to pass through, it is possible to determine the size of the emulsion particles.

Determinations made on these lines have shown that the globules in a typical oil emulsion may be smaller than the micron, that is less than one thousandth of a millimetre. Lewis has stated that in stable emulsion of oil in water the particles are not larger than 0.4 of a micron in diameter. These figures show that the emulsion particles are larger than the colloidal particles in a colloidal solution but the differences are not sufficiently large to place the two classes of particles in different orders. It is in fact probable that there exists a regular gradation in the dimensions so that the largest colloidal particles approach the size of the smallest emulsified particles. In other words there is no clear line of demarkation between the dimensions of colloidal and emulsion particles. Several facts support this theory. Emulsion particles are subject to the Brownian movement in the same way as colloidal particles, that is, seen under the microscope, the emulsified particles and the colloidal particles, instead of moving in the liquor in straight lines up or down according to whether they are lighter or heavier than the liquid, they move jerkily with a to and fro motion in any and every direction. The Brownian movement is also experienced by bacteria and other minute bodies. One explanation is that liquids are composed of elastic molecules in constant motion. These incessant movements of the molecules of the liquid, acting upon the insoluble particle, i. e., the emulsified particle, or the bacterium, do not exactly neutralize one another but exert a localized action on the particles, causing them to move first one way and then another.

In the second place the emulsion particles as well as colloidal

particles are subject to movement under the influence of the electric current. In other words if an electric current be passed through an emulsion, the particles are driven from one and attracted by the other terminal. Usually the particles coalesce at the terminal to which they are attracted, in the same way as colloidal particles will often coagulate under the same influence. Emulsion particles, therefore, like colloidal particles, possess a definite electrical charge both as regards quantity and sign.

This electrical transport of emulsified and colloidal particles is only a particular case of the electrical transport of very fine powders suspended in a liquid, a phenomenon discovered by Faraday. A particle of any substance, solid, liquid or gas which is fine enough to remain in suspension in a liquid, moves in the liquid when a current is passed through. For a given substance in a given liquid the direction of movement is independent of the size or shape of the particle. The rate of movement is proportional to the strength of the current.

Although the Brownian movement and the phenomena of electrical transport just mentioned, create a certain analogy between the emulsion form and the colloidal form, yet there are quite different characteristics such as (1) the absence of the gel form in emulsion, (2) the slight sensitiveness of emulsions to the action of electrolypes, (3) emulsions may be either of liquids or solids whilst colloidal particles are never conceived of as solids.

Effect of Surface Tension

There is not space to describe in detail the meaning of the term surface tension. It is the force which keeps two liquids such as oil and water from mixing with one another. It is connected with the attraction of the molecules for one another at the surface. All the molecules in a liquid are in motion to and fro. They are held together by powerful forces of attraction for one

another so that the distance which a molecule travels before colliding with another molecule is not great. The molecules are continually colliding with one another. In solids the motion of the particles is greatly hindered by adjacent molecules and one molecule can only get away from contact with another molecule extremely slowly, if at all. The molecules in a solid have only very limited mobility and therefore a solid retains its shape indefinitely. The only difference between a solid and a liquid is that in the latter the molecules have greater freedom of motion and can travel from one part of the liquid to another. They have sufficient freedom to allow the liquid to assume the shape of the vessel into which it is put but the freedom of motion is not as great as in gases in which the molecules seem to be able to travel much more independently of one another. In a liquid the molecules are much more compact than in gases, or in other words in gases the spaces between the molecules are much greater than in solids. The closeness together of the molecules in a liquid causes them to be subjected to strong inter molecular attraction so that the liquid assumes a definite volume. In a gas the molecules are so independent and rapidly moving that the gas has no definite volume, but exerts a pressure and will fill any empty space. The assumption by a liquid of a definite volume gives it a definite boundary or surface. Since the molecules in the body of a liquid are attracted by the other molecules equally in all directions it follows that at the surface the attraction is greater inwards than outwards, because the molecules of the liquid below it will attract it more powerfully than the molecules of the air above. This produces at the surface the forces called surface tension. This excess of attractive forces at the surface gives the liquid its definite boundary between itself and the atmosphere. In this sense the surface tension may be regarded as a skin or scum which holds the liquid together. Some of the molecules at the surface may be assumed to be traveling with a sufficiently high velocity to leave this surface. If the

velocity be high enough, the molecule will get beyond the range of attraction of the molecules in the liquid and will pass into the space above and not return. (This is the explanation of the evaporation of water or other volatile liquid.) If the velocity of the escaping molecule be not high enough to carry the molecule beyond the sphere of attraction of the other molecules, its upward velocity will become lower and lower until it ceases and will then be attracted back again into the liquid. In a volatile liquid such as alcohol the proportion of the molecules with high enough velocities to escape from the surface is great whilst in a non volatile liquid such as oil the proportion of these rapidly traveling molecules is small. Raising the temperatures will increase the velocity and therefore increase the rate of evaporation.

When two liquids are placed together a similar thing may occur, that is the two liquids may exert a definite surface tension between one another in the same way as the surface tension between a liquid and the air as already described. Between oil and water, for instance, there is a marked surface tension. Between alcohol and water on the other hand there is no surface tension. If a layer of alcohol be poured gently on to a layer of water and the two left to stand, in time there will be no line of separation or boundary between them. This is because the attraction of the alcohol molecule for the water molecule is as great or greater than either that of the alcohol for alcohol or water for water. A molecule of water therefore rising to the surface between the water and alcohol will be just as likely to pass into the alcohol as to be attracted back again into the water. These two liquids are therefore miscible with one another in all proportions. There are other possibilities between the cases of alcohol and water and oil and water. For instance water and chloroform, each of which is slightly soluble in the other. If these two liquids be shaken together they will separate out again but there will be a little water in the

chloroform and a little chloroform in the water. In these cases it must be assumed that when a certain number of water molecules have passed from the water to the chloroform, there is just as much tendency for them to return to the water, as for more molecules to pass into the chloroform.

To return to the case of oil and water, although practically no admixture takes place and although each liquid retains a considerable surface tension at the dividing surfaces yet this surface tension is less than that between the oil and the air. It is this factor which makes the presence of water in leather necessary for the successful application of oil or grease, because the surface tension between oil and water is less than between oil and air. Oils which exert low surface tension between themselves and water are the ones which will most easily penetrate wet leather. Degras and cod oil have low surface tension and Procter attributes to this the value of degras in rapidly penetrating leather and in conferring this property upon the other oils and fats with which it may be mixed in stuffing mixtures.

Not only have different oils very different surface tensions but the latter may also be affected by outside influences. For instance, raising the temperature reduces the surface tension, so that the greater ease with which a stuffing mixture will penetrate leather when it is warm than when it is cold is due not only to the more liquid condition but also to the reduced surface tension at the higher temperature.

The nature of the leather itself may also have some influence on the ease of penetration. Certain tannages produce leathers which are sometimes said to carry grease well. Such tannages are therefore much sought after for currying purposes. The reason for the more ready absorption of greases lies probably in the surface tension of the wet fibre with regard to oils as well as upon the extent to which the fibres are isolated.

In the process of fat liquoring, the surface tension of the oils employed is very considerably reduced by the presence of

soap. Just as a layer of soap on the hands will enable oil to be spread over them, that is, will prevent the oil from gathering together in drops, so the presence of soap in a fat liquor not only enables the particles of oil to be very finely divided but also to spread more easily over the fibres. The ease with which a fat liquor penetrates leather compared with an ordinary oil is therefore largely a question of reduced surface tension.

That the mechanical action in fat liquoring is not responsible entirely for the more rapid penetration of the oil is shown by the fact that if the leather were drummed in the oil not in the form of an emulsion or fat liquor, the oil would not penetrate. It is the emulsification of the oil or the division into very fine particles and also the low surface tension of the oil as regards the wet fibre, which make the penetration of the oil in fat liquoring so much easier than when merely applied to the surface or in the form of an ordinary oil.

Effect of Surface Tension on Oil Emulsions

All oils are not equally easily emulsified under similar conditions. What therefore is the property of an oil which determines whether it is emulsified with ease or with difficulty? Surface tension exerts the most important influence. The question resolves itself into one of making large globules into small ones. The ease which a globule A will break up into two globules, a, a', determines the ease with which the oil can be emulsified. The globule A begins to lengthen out, then to be restricted at the middle and finally the two parts are separated and two smaller globules a and a' are formed. What is the force which resists the splitting up of the particle A into two particles a and a'? The splitting up is accompanied by an increase in the surface area. The surface area of one particle, assuming it to be spherical, is smaller than the area of two particles made from it. The force, therefore, which resists the increase in surface is the one which influences the ease or

otherwise with which an oil is emulsified, and this force is surfsce tension, of which seme account has already been given. The surface tension between oil and water acts as though there were an elastic membrane round each globule which opposes any increase in the area of the external surfaee. The surfaco tension, therefore, at the separation surfaee between the oil and the water, resists the formation of an emulsion and the higher the surface tension the greater the resistanee. Reversely tho change from the form a and a' to the form A, that is, the breaking of the emulsion is the more readily brought sbout, the higher the surfaee tension between the oil and the water.

It follows, therefore, that the lewer the surfaee tension of the oil the mere easily the oil will be emulsified and the more stable will he the emulsion, ether things being equal.

In order to measure the surfaee tension between the various oils on the ene hand and different media sueh as water snd soap solutions on the other hand, Meunier adopted the method of Tate, which consists in measuring the number ef drops of the liquid per unit of weight whieh are formed as the liquid is allewed to pass through a narrew orifice from one vessel into the ether liquid.

Meunier used an ordinary burette. The height of the liquid in the burette was maintained eonstant. The capillary opening whieh was constant was immersed in the liquid. By allowing the oil to run from the burette into water and by counting the number of drops per unit weight of the oil, it is possible to compare the surface tension of the different oils under different eonditions.

The number of drops obtained under these eonditions aro inversely proportional to the surface tension, because the higher the surfaee tension the less readily does the liquid break up into drops.

The number of drops per gram obtained when some of the common oils were allowed to drop into water were:

Castor oil 9, mineral oil 9, linseed oil 18, neatsfoot oil 18, and olive oil 20. Contrary to one's expectations the temperature does not affect the surface tension by this method to any marked extent, although viscosity diminishes very rapidly as the temperature is raised.

Mineral salts, which have such a harmful effect on emulsions made by means of certain colloids such as soap, actually help emulsification when dealing with pure water emulsions. Thus, using the above method one gram of neatsfoot oil in pure water gave 18 drops, in a 1 per cent salt solution 19 drops, in 5 per cent salt solution 24 drops, and in 10 per cent solution 31 drops.

Solutions of alkaline sulphoricinates such as the ammonium salt of sulphonated castor oil have a very marked action on the surface tension between oil and water.

Thus in pure water, neatsfoot oil gave 18 drops, in a 5 per cent sulphonated castor oil solution 29 drops, in a 20 per cent 50 drops and in a 50 per cent 107 drops whilst in a 60 per cent solution the neatsfoot oil did not form drops at all but ran in a continuous stream. The effect of the sulphonated oil depends largely upon the extent to which it has been neutralized. If it be slightly acid, as commercial sulphonated oils often are, the effect on the surface tension and upon the emulsification is much slighter than if neutral or slightly alkaline.

Effect of Sulphonated Oils Upon Surface Tension

This effect of the sulphonated oil upon the surface tension is explained (1) by the hydrolyzing and saponifying action of the sulphonated oil, and (2) by the colloidal character of the solution of the sulphonated oil.

That the sulphonated oils have a hydrolyzing action upon other oils is explained by analogy with other sulphonated

compounds. Thus mono-sulphonic benzine has remarkable hydrolyzing properties on oils when boiling. Industrially Twitchell's reagent is used for hydrolyzing and saponifying oils and fats. The composition of this reagent is secret but it is probable that it is formed by the action of sulphuric acid upon fatty acids in solution in naphthaline, or in other words that it is a sulphonated compound; 1½ to 2 per cent of this reagent upon the weight of the fatty matter is sufficient to hydrolyze the latter into free fatty acid and glycerine.

Lewowitsch has shown that the same hydrolyzing power is possessed by other sulphonated organic compounds so that it is reasonable to suppose that a sulphonated oil such as turkey red oil owes some of its power of emulsifying other oils and fats to its similarity to these other sulphonated compounds, that is to its power of hydrolyzing oils and fats.

The action of the alkaline salts of a sulphonated oil upon the surface tension of another oil is much stronger than that of other sulphonic derivatives such as mono-benzine-sulphonic acid, or its sodium salt on the sodium salt of disulphonic a-naphthol.

Sulphuric acid itself has an effect by lowering the surface tension. Thus olive oil falling into pure water gave 20 drops, into a 2 per cent solution of sulphuric acid 25 drops, and into a 10 per cent solution 33 drops.

This slight effect corresponds to a slight hydrolysis, which is nevertheless sufficient to produce an emulsion when olive oil is agitated with sulphuric acid.

It is even possible to produce an emulsion with water alone owing to the slow hydrolyzing action which is favored by the gradual division of the oil and increase of the surface exposed. The agitation with water alone must of course be prolonged in order to produce any appreciable hydrolysis. This aqueous

emulsification is rendered much more rapid if the oil is itself slightly acid.

The effects on the surface tension are less marked with sulphonated oils than with solutions of alkalies such as soda.

The Influence of Colloids on Oil Emulsions

It has already been pointed out that the emulsified particles of an oil emulsion are of greater dimensions than the particles of a colloidal solution, therefore in an oil emulsion prepared in the presence of a colloid, each emulsion globule will exert an attraction for the colloid particles in its neighborhood so that each emulsion globule will become coated with a covering of the colloid particles which will constitute a protective grain and will prevent the emulsified particles from coalescing. An emulsion of an oil therefore in the presence of a colloid always shows pronounced stability.

The colloid gives a certain viscosity to the emulsion medium which helps to keep the globules in suspension by opposing their upward movement due to gravity.

Milk and egg yolk are types of emulsions formed by the help of colloids. The oil globules are surrounded by colloid albuminous matter, in the case of milk by casein, and in the case of egg yolk by cholin. The use of such substances as gums, gelatin, Irish Moss in the making of oil emulsions both for industrial and for pharmaceutical purposes depends upon their colloidal effect in the manner just indicated.

The Action of Very Fine Emulsions Upon the Emulsification of Oils

The similarity between fine emulsions and colloids has already been described. It is not surprising therefore that the two have the safe property of helping emulsification or other substances.

Thus if instead of using water as the medium for emulsi-

fying an oil, a fine emulsion be used it is easy to see that the step is likely to produce a more stable emulsion. The original fine emulsion will behave in the same way as the colloidal particles, that is, they will coat the new emulsion globules with a protective coating, rendering the coalescence more difficult.

The two substances may be emulsified together or preferably the oil should be emulsified in the previously formed emulsion of the very fine particles.

An interesting case from this point of view, which is dealt with more fully elsewhere in this article, is that of the emulsification of a neutral oil in the presence of its fatty acid. It has been known for a long time that an oil which contains much free fatty acids, such as a rancid olive oil, is much more easily emulsified than a fresh neutral oil. The free fatty acids, the products formed when an oil becomes rancid, possess much stronger emulsified properties than the neutral oil and it is possible to obtain, by suitable methods of agitation, very stable emulsions with fatty acids and water alone.

With a rancid oil, such as olive, there is no doubt that the ease of emulsification is due to the protective effect of the fine emulsion of the fatty acids upon the neutral oil globules. The stability of such an emulsion is due to a protective covering of the neutral oil globules by the smaller fatty acid particles.

Quite apart from this action the surface tension of a neutral oil in contact with water is much higher than in the presence of the fatty acid of the oil, thus with a neutral neatsfoot oil the number of drops obtained was 30, whilst with equal parts of neutral oil and free fatty acid the number was 44 and with free fatty acid alone 62.

The effect of alkalies upon the surface tension of an oil is very marked. A very small trace of alkali in the water will very appreciably diminish the surface tension. Thus in one test, neatsfoot oil into pure water gave 13 drops, whilst into water containing 0.02 per cent of caustic soda, i. e., 1 part in 5000, it

gave 21 drops, and into water containing 0.06 per cent, that is 1 part in 1660, the oil dropped in a continuous stream. A small amount of a strong alkali such as caustic soda has therefore a very strong action on the emulsification of an oil and very many fat liquors contain free alkali which has been added to render the emulsification easier and to make the emulsion more stable. The advantages and disadvantages of the presence of free alkali in a fat liquor are discussed elsewhere in this article.

Since both colloids and fine emulsions exert a favorable influence on the emulsification of oils it is only natural that when the two are present together the effect is more pronounced than when they are alone. Egg yolk, which is one of the finest emulsifying agents for oils, depends for its action upon the fact that it contains a colloid (albumen or lecithin) and a fine emulsion (the egg oil.) Similarly milk is a good emulsifying medium for oils. Milk contains both a fine emulsion (cream) and a colloidal solution (casein). Olive oils are often allowed to become rancid by the addition of albuminous substances; the rancid oils being readily emulsified and possessing emulsifying properties upon other oils. The rancid oil probably contains some of the albuminous matter in the form of a colloidal solution, whilst fatty acids (which readily form an emulsion) are produced as the oil becomes rancid.

Formation of Emulsions by Means of Soap

Solutions of soap may be regarded as colloids and they exert a very strong effect on the formation of stable emulsions of oils.

In dealing with the effect of soap on the formation of stable emulsions one of the first things to be considered is the ratio of alkali to fatty acid in the soap and the effect of varying this ratio upon the power of soap to produce oil emulsions. (An outline of the composition of soap has already been given.) Maunier found that the ratio of alkali to fatty acid which gave

the best results varied with the dilution of the emulsion. Thus the proportion of alkali to fatty acid is higher the more dilute is the emulsion. In many cases an excess of alkali is a disadvantage and an excess of fatty acid an advantage. When soaps which contain an excess of fatty acids (that is more fatty acids than correspond to the alkali) are dissolved in water, the effect is to produce a colloidal solution of the true soap and a fine emulsion of free fatty acids. It follows, from what has been said in the preceding paragraph, that the presence of a colloidal solution together with a fine emulsion helps to produce a stable emulsion with an outside material such as a neutral oil.

In such a case where there is a deficiency of free alkali in the soap, the latter should be dissolved in as small a volume of water as is possible and the oil added to the strong soap solution. The dilution should be effected after the oil has been added to the soap. The use of soaps containing an excess of free fatty acids may be convenient for the preparation of those emulsions which must have an acid reaction.

If some substance such as common salt, which will precipitate a colloid, is added to an emulsion of an oil and soap the whole emulsion will be thrown out. The salt throws out the colloidal solution of the soap and thus the emulsion is destroyed. It is for this reason that fresh egg yolks are to be preferred to preserved or salted egg yolks, for the making of emulsions for use as fat liquors upon chrome leather.

When neutral soaps are used for making emulsions, they are hydrolized in water to a certain extent to yield alkali on the one hand and free fatty acid on the other hand. The free alkali exerts its powerful emulsifying properties upon the oil. In this case there are three agents helping to produce emulsification, alkali, the colloidal solution of the soap, and the fine emulsion of the free fatty acid.

Potash soaps, that is, soft soaps have stronger emulsifying properties than soda or hard soaps.

Soaps which contain salt are to be rejected for the making of emulsions for the reason just outlined.

Formation of Emulsions by Means of Oil Solvents

If a solid or liquid substance which is insoluble in water be dissolved in some other liquid which is miscible with water and if this solution be then poured into water, emulsions are usually produced which are very stable. Thus if an oil be dissolved in alcohol and this solution be poured into a large volume of water the oil is thrown out of solution in the form of an emulsion. Unfortunately very few oils with the exception of castor oil are soluble in any solvent which is miscible with water. A similar sort of thing is obtained by a mixture of a sulphonated oil with carbon tetrachloride. If the oil to be emulsified be made into a creamy paste by adding to the above mixture, a product is obtained which diluted with water yields a very permanent emulsion.

The Action of Ferments in the Formation of Emulsions

Since the emulsifying properties of an oil are in proportion to its acidity, it follows that any factors capable of developing this acidity will increase the emulsifying properties. Von Tiechem, many years ago, observed that when any substance containing water was immersed in oil, the surface of this substance became covered with a profuse vegetative growth of mould, particularly the common green mould, penicillium glaucum. Amongst the filaments of the mould white nodules of another substance were found, which proved to be the fatty acid. The production of fatty acids was caused by the decomposition of the oil by means of the ferment contained in the mould.

The saponifying engymes or lipases which are secreted by certain bacteria behave much more energetically in the presence of other fermentations of sugary or nitrogenous matter. This is one reason why the acidity of oils as well as their emulsify-

ing properties increase in the making of chamois leather. The organic matter of the pelt furnishes the nitrogen for the fermentation of the oil.

Objects of Fat Liquoring

The primary object of fat liquoring leather is of course the incorporation of oil on the films of the leather. Before discovering the other objects and also how the effects produced by fat liquoring differ from those produced by oiling the surface or by drum stuffing, it will be well just to outline the method of application of the fat liquor to the leather, postponing for a moment the details of the process. The process is carried out by motion, the emulsion is not applied by hand to the leather, but the latter is drummed or turned in the paddle with the fat liquor. The mechanical action of the drum helps the oil to be absorbed by the leather.

The leather in the tanned state but not dried as for drum stuffing is put into the drum. The emulsion is then poured in through the axle while the leather is being turned. The process is usually carried out at about body temperature for vegetable leather and at higher temperature for chrome leather. The oil is gradually absorbed by the leather and in half an hour or so the whole of the oil should have been removed from the liquor leaving nothing but clean liquor.

The process therefore differs from both oiling and drum stuffing although it is perhaps a hybrid of the two. It differs from oiling in that motion is applied and that the oil is driven in whilst the leather is still wet. (In oiling the oil is only absorbed as the leather dries.) It differs from drum stuffing in that the amount of water is not so vital since an excess is usually present. In drum stuffing the leather must itself be partially dried and of course the grease is applied in the free form, that is, without water. Emphasis has been laid several times on the importance of the correct adjustment of the

amount of moisture in the leather before drum stuffing. In fat liquoring, the oil is applied with a large excess of water so that the amount of moisture in the leather is not so important. (It is true that some workers squeeze or partially dry the leather before fat liquoring and also adjust the amount of water in the fat liquor so that the whole of the oil and the water is absorbed in the drum, but generally speaking the objects of fat-liquoring are best achieved by having the leather wet and the fat liquor containing sufficient water so that after fat liquoring, clear water remains in the drum. The former plan may make the absorption of the oil easier since the fat liquor can be taken up bodily, instead of the leather having to exercise a selective absorption for the oil from the water.) Another main difference between fat liquoring and either oiling or drum stuffing is that in the former soap is taken up by the leather and this may play an important part which will be discussed later. The above are therefore the main points which distinguish the process of fat liquoring from oiling the grain and from which arise the special advantages of the one over the other.

Advantages of Fat Liquoring Over Oiling

(1) Speed. The most obvious advantage is that of speed. In oiling, each piece of leather has to be treated separately. In fat liquoring the oil is applied in one mass to many pieces of leather. The oil in fat liquoring is absorbed in half an hour; with leather which has been oiled the absorption is dependent upon the drying of the leather and may take days. The saving of labor in handling the goods is also very considerable.

(2) Uniformity. In oiling, only the surfaces receive the application of the oil and although the oil is absorbed or drawn in as the leather dries yet it cannot very easily be absorbed and distributed evenly throughout the whole piece of leather. It is also of course very difficult to regulate the amount of oil to suit different thicknesses of leather. In fat liquoring, the

oil is driven right to the interior of the leather so that all the fibres are lubricated evenly. When oiling by hand it is difficult to give definite quantities of grease, whilst in fat liquoring the amount can be gauged quite accurately on the weight of the leather.

Softness of Leather

The fact that in fat liquoring the oil is distributed evenly throughout the leather renders the leather produced much softer than a corresponding amount of oil would do if applied by hand. The effect of even a very small amount of oil in softening leather and making it flexible when applied in the form of a fat liquor is very striking. For instance a leather which has been fat liquored so as to contain 5 per cent of oil when dried and finished may be extremely soft, whereas if the same amount of oil had been applied by hand the leather would be much less soft or flexible. This is the great advantage of fat liquoring over any other process of incorporating oil in leather that a very small amount will make the leather soft and flexible. There are many cases where a leather is required extremely pliable but which must not contain much grease. For instance, modern shoe upper leather. These must, of course, be mellow and flexible yet they must not contain much grease or the leather would not take on the high polish which is demanded. The process of fat liquoring allows these two objects to be achieved in a way which no other process would give. The greater softening powers of a given quantity of oil when applied in the form of a fat liquor than when applied to the surface by hand, must be ascribed to the more finely divided condition in which it is applied to the leather as well as to the fact that the mechanical action of the drum makes the oil penetrate more readily to the interior of the leather.

Color

The color of leather which has been fat liquored will generally be lighter and more uniform than one which has been oiled, although this is not true of very heavily tanned leather in which the oil on the surface exerts a protecting action against oxidation and darkening. The process of fat liquoring is not usually applied to heavily tanned leather for the object of maintaining a light color. For this purpose a coat of oil on the grain is more suitable since the latter produces its effect by remaining on the surface and preventing the soluble tanning matters from coming to the grain. A fat liquor applied in this case would not answer the purpose because not only would the oil penetrate into the leather, but being carried out with excess of water some of the soluble matters will be removed from the leather. The point referred to, that the color of fat liquored leather is lighter than that of oiled leather, applies to dyed leathers. Leather to be dyed should not contain free oil on the surface, not only so that the darkening effect of the film and oil should not come into play but also in order to render the dyeing process itself easier. Oil on the grain of the leather before dyeing will tend to prevent the dye from striking easily and evenly. Since dyed leathers are required soft and flexible and since the presence of oil is necessary to this end, the oil must be applied in such a way that the grain is left free from a film of oil. The process of fat liquoring enables this to be done. The fat liquor may be given either before or after dyeing and if done satisfactorily the color of the final leather will be even. If the fat liquor is applied before dyeing the oil should thoroughly penetrate the leather so that the process of dyeing is not made difficult. If the fat liquor is applied after dyeing, since the leather can be dyed in the quite grease free state, the leather should similarly be even in color, although precausions must be taken that the fat liquor does not remove, or strip or affect the dye.

The process of fat liquoring is not given with a view to increasing weight so that no comparison of its advantages over drum stuffing can profitably be given. Its main use is in making leather soft and supple without the use of large quantities of oil. This is of special value (1) in leathers which are to be dyed and in which an excess of oil would darken the color and make it uneven, (2) in leathers to be glazed, such as modern shoe upper leather in which the presence of grease on the surface would prevent a high polish.

Although the process of fat liquoring is not often used with a view to obtaining great weights yet it should be pointed out that by this method it is possible to incorporate large quantities of oil without making the leather feel or appear greasy. Much larger quantities of oil can be incorporated in leather by this means than by any other without producing greasiness. Drum stuffing and dipping processes allow large quantities of grease to be absorbed without greasiness but in these cases it is due to being able to use hard greases of high melting point. In fat liquoring the property is not due to the use of hard greases, because the material is liquid, but is due to the fineness of division of the oil and the fact that the finest fibres are coated with the oil. It may be asked how it is that of two leathers containing exactly the same amount of oil, one of which has been fat liquored and the other one merely oiled or hand stuffed, the former will be more or less greasy in feel and appearance than the latter. It is due entirely to the fineness of division. Professor Proctor writing on the influence of moisture, etc., on the penetration of oils and fats into leather says, "It may be concluded that oils and fats have little power in themselves of isolating the fibrils, and that this must be accomplished by other agencies, since if they are still adhering together, the fats cannot penetrate them. Hence the necessity of moisture, and the importance of powerful mechanical treat-

ment, which will work the minute globules of oil between the fibrils. In the case of tanned leathers, the last condition is less important, since the fibres are already isolated by the tannage, and capillarity assists the penetration. Even in this case the distribution of the fat is much assisted if it is already in a state of fine division or emulsification, and if the surface tension between it and water is low."

It will be seen that a fat liquor presents just the right conditions for this completion penetration of the finest fibrils. The oil is itself in an extremely fine state of division, and the mechanical action of the drum assists the penetration by forming the oil through the spaces and by the constant movement of the fibres over one another.

When the oil is not completely split up in the leather over the whole fibres but is present in larger drops than it can be more easily squeezed out, and the leather both feels and appears greasy, but when it is thoroughly emulsified and therefore adherent to the fibres it cannot be expelled by mechanical means and the leather does not feel greasy.

It is for this reason that by fat liquoring, large quantities of grease can be incorporated and the leather yet remain not greasy.

The penetration of oils and greases is also dependent upon surface tension as well as upon the fineness of division.

Class of Oils Used in Fat Liquoring

Most of the common oils can be made into the form of emulsions by means of soap so that it is not surprising that recipes for fat liquoring leather include the use of very diverse kinds of oil, although two or three stand out above the rest as being most suitable for application to leather. Every leather dresser has his own special formula for making a fat liquor which he usually invests with wonderful properties and which he regards

as giving results unobtainable by any other fat liquor. A list of these special fat liquors would fill a book so that only examples or types will be given.

The class of oil used will depend upon the class of leather to be treated. A leather to receive a high glaze will require a different fat liquor from one to be finished dull.

Perhaps the first fat liquor to be used in leather making was egg yolk. This was used in connection with alum tawing and helped to give softness and fullness. Egg yolk is really an emulsion of oil in water together with a certain amount of albuminous matter. The amount of oil is about 30 per cent and it very closely resembles olive oil in chemical properties. When the Dongola tannage or a combination alum and gambier tannage was first introduced, it owed its success largely to the use of the alkaline liquor which is obtained when the surplus oil is washed from chamois leather. As already mentioned, in the making of chamois leather the skins are impregnated with cod or seal oil which is allowed to oxidise partially. The excess of the oil is washed out by means of soda and when freed from the soda is called sod oil. This oil contains a proportion of water and owes much of its success as an oil for application to the leather, to the fact that it is readily emulsified with water. The alkaline liquor itself before separation of the oil will be a very good emulsion and as such will be readily absorbed by leather. The use of this material in the combination tannage of alum and gambier was perhaps the first direct use of an artificial emulsion and opened the way to the modern practice of fat liquoring. It would soon be found that this alkaline liquor from chamois leather making owed its property of being readily assimilated by leather to its emulsion form and from this it would only be a short step to the use of emulsions made from oil and soap which nowadays form the bulk of the fat liquors.

Drying oils such as linseed are generally regarded as unsuitable, and most observers agree upon this. With regard to

oils such as neatsfoot opinions differ widely. Neatsfoot oil is a very common one in England as a materiel for use with fine leathers, but Eitner warns against its use on the ground that it is liable to cause a white spue and also to give the leather a disagreeable smell.

Degras and sod oil are perhaps as suitable and as widely used as any, particularly where softness is desired. These materials are themselves emulsifiable even without the addition of soap, and they are also capable of transmitting their emulsifying properties to other oils so that they are very often used in fat liquors along with other oils. Fish oils are sometimes regarded as unsuitable although in use upon vegetable leather they may give good results. As a rule fish oils do not give as satisfactory results upon chromo leather as such oils as castor or neatsfoot and olive which are perhaps the commonest oils for fat liquoring chrome leather. Mineral oils as a class are not as valuable as vegetable oils. They can be made to emulsify quite readily and they possess good lubricating properties but they do not possess the same feeding properties, that is, they do not give the same feeling of fullness as vegetable and animal oils. They are, however, often used as constituents of fat liquors along with other oils.

Most of the commercial ready made fat liquors contain a proportion of mineral oil. The so-called soluble oils (they are not soluble in the true sense of the term, for they do not dissolve in water to form a clear solution, but when poured into water they form a stable but milky emulsion without separating out again as would an ordinary oil) very often contain some mineral oil. The presence of the emulsifiable oil confers upon ordinary oils the property of being emulsifiables so that if a proportion of a self-emulsifiable oil, such as sulphated castor oil, be mixed with mineral oil the mixture becomes self-emulsifiable. Most of the commercial "soluble" oils take advantage of this fact and contain only a proportion of a true self-emulsifiable oil.

Castor oil makes an excellent fat liquor particularly in conjunction with a castor oil soap. Such a fat liquor is especially useful for leather to be glazed because it interferes with dyeing and glazing less than most other oils; in fact factor oil alone, according to Procter, may be used to oil boots in such a way that they can immediately be blacked and polished.

The condition of the oil with regard to rancidity also has a great influence on the fat liquor made from it. An oil containing free fatty acids will emulsify much more readily than a pure glyceride; thus, with olive oil which rapidly becomes rancid and therefore unsuitable for lubrication, the acidity actually helps the oil to be emulsified and gives it an advantage over a neutral oil for fat liquoring purposes. The acidity and the ease of emulsification are sometimes actually increased by the addition of a little oleic acid and formerly when olive oil was used as a Turkey Red oil, it was purposely allowed to become rancid to such an extent that it contained much more than 25 per cent of free fatty acids.

Class of Soaps Used

Most soaps belong to one of two classes, hard and soft. Both of these classes are similar chemically, that is they are both salts of fatty acids. At the beginning of the article a brief summary was given of the chemical composition of oils and reference was made to that of soaps. As this question is important to a proper understanding of some of the side issues of fat liquoring, it may be well to recapitulate. The true oils and fats (which alone can furnish soaps) may be regarded as compounds between glycerine as the base and fatty acids as the acid portion of the salt. When such oils are hydrolysed or saponified, which can be carried out either by steam or by means of alkali, the glycerine is split off from the fatty acid. If the hydrolysis has been produced by steam, the fatty acid itself is left. This is either an oil or a solid fat such as stearic acid. If the hydrolysis has been brought

about by alkali (which is strictly the only case of saponification) the fatty acid is not present in the free form but as an alkali salt of the fatty acid. Thus if caustic soda or washing has been used to bring about the hydrolysis the resulting product will be a sodium salt of the fatty acid. If caustic potash or potassium carbonate has been the alkali the product is a postassium salt of the fatty acid.

Thus, to take a typical case, sodium stearate or the sodium salt of stearic acid,

$C^{17}H^{35}COOH$	$C^{17}H^{35}COO\ Na.$
stearic acid.	sodium stearate.

The sodium salts of the fatty acids comprise the hard soaps, and the potassium salts the soft soaps. (This was perhaps more strictly true before the war, but nowadays certain soft soaps are on the market which contain no potassium at all). Some of these so-called soft soaps are soda soaps which in the ordinary way would be hard, but which are made pasty by excess of water. Instead of containing about 20 to 30 per cent of water as a good hard soap should, some of these so-called soft soaps contain over 80 per cent of water. Such a soft soap could easily be made from an ordinary bar of soap by letting down with water and would probably be two or three times as cheap as the bought variety. As the commonest use for soft soap is as a detergent, many of these watered down soaps contain in addition to the soap an excess of free alkali. The alkali has strong cleansing and grease removing properties and the value of such a compounded soft soap for cleaning purposes would not probably be distinguished readily from a genuine potash soap. From the point of view of fat liquor making, however, such a soap would have a vastly inferior value to the genuine article. As will be shown later the soap in a fat liquor plays a definite function apart from its emulsifying properties. If then the same quantity of such a watered soap be taken as would be taken of a genuine potash

soap the emulsifying properties might be satisfactory, but the actual weight of soap present in the fat liquor would be too little and some of the effects sought for in adding soap to a fat liquor would be lacking. It is possible, however, to produce a soda soap which is soft even without a great excess of water. By combining the alkali with a liquid fatty acid the soap produced may be soft. The whole of this question has arisen from the shortage during the war of potash salts of which Germany had almost a monopoly.

Influence of Amount of Soap

Not only has the kind of soap used an effect on the fat liquor and upon the leather but the proportion of soap in the fat liquor may also have an influence. A correct proportion of soap will give a feeling of fullness which is not obtained without soap whilst an excess of soap will produce a leather difficult to finish. M. C. Lamb states that if too much soap be used the resulting leather is dull, heavy and flat feeling. An excess of soap is particularly to be avoided if the leather is to be glazed or rolled because it may cause a cementing together of the fibres which will produce the objectionable dead feel.

The effect of too much soap will make glazing difficult as of course will an excess of oil. The amount of soap should generally be just sufficient to produce a stable emulsion with the oil used.

The choice between a hard soap and a soft soap for fat liquoring purposes is almost entirely a question of individual preferment. Most of the adopted methods have been based upon empirical grounds. Thus a worker will have discovered that a given proportion of a certain oil mixed with a given proportion of a certain soap have produced a good emulsion and one which is absorbed readily. It is very difficult indeed to frame any general rules as to the suitability of any given oil or soap. The question is complicated by the differences which exist in

the general methods of leather making. What a certain fat liquor will do with one set of conditions might be done by a quite different one under different conditions. In other words the same fat liquor under different sets of conditions will produce quite different results. The conditions which will alter the effects of a fat liquor are such things as the nature of the tannage and the subsequent treatment of the leather. The leather trade is perhaps unique in that the methods of treatment are never uniform. Not only are there very wide variations in the class of leather produced by different manufacturers so that the resulting leathers are quite individualistic and so that it is possible for an expert to say "That is so-and-so's leather" but also it is possible for tanners to get similar products by quite different means. The whole sequence of processes must be taken into account, each process depending upon the previous one, and having itself a bearing on the processes which follow. For instance, a leather which has been tanned in weak mellow liquors and which is naturally soft and flexible will not require as much fat liquors as one which is hard and harsh. If the same fat liquor be given to both cases the results will not be the same. It is therefore not possible to lay down hard and fast rules for the composition or amount of fat liquor required for any class of leather and it is generally useless for a tanner to attempt to duplicate another's method in merely one step of his process. By merely altering one stage of the process it may be found that many of the succeeding ones are thrown out of gear and must themselves be modified or adjusted to adapt the whole sequence of processes to produce the correct result. To take a case in point. A leather dresser may be giving a certain fat liquor followed by a definite combination of dyestuffs to produce a given shade of color, but he may be doubtful about the softness or toughness of his leather. He ascribes this to the fat liquor and he therefore alters its composition. He may change

the soap or the oil or both or give a quite different type of fat liquor, that is instead of giving an oil and soap fat liquor, he may give an acid fat liquor, that is a sulphated oil fat liquor. By giving the same method of dyeing and the same combination of dyes it will probably be found that the final shade of leather is quite different, and that to get the original shade of color it may be necessary to give a quite different mixture of dyestuffs.

Formulae for fat liquors, although of interest as types, should not be taken too rigidly.

In connection with the difference between a hard and a soft soap for fat liquoring, M. C. Lamb says, "that the use of a hard soap is generally speaking not to be recommended in fat liquoring operations especially when a maximum of softness is required. A hard soap cements the fibres of the leather together as it were, particularly if there is an excess of soap. The resulting leather is flat and devoid of the plump soft elastic feel that a properly fat liquored leather possesses, and this is markedly the case if the goods are subjected to heavy pressure in glazing. The soap that is a component part of a fat liquor should be a soft (potash soap) which has not the tendency just mentioned to harden the leather even if by mischance the goods are over fat liquored. Soft soap oil emulsions are moreover more easily prepared than hard soap emulsions."

Various attempts have been made to account for the absorption of the oil and soap from a fat liquor. The soap does not merely serve to keep the oil in the emulsion form but is itself absorbed by the leather. It may seem strange that a substance which is so soluble in water as soap should be removed by leather, and it is not surprising therefore that theories have been put forward that the soap actually combines with the leather or acts upon some constituent of the leather.

Thus one theory states that (in the case of chrome leather which was the first to be fat liquored) the soap combines with the chromium in the leather to form a chrome soap.

J. B. Salamon says that the generally accepted view is that the soap becomes hydrolyzed into its alkali and fatty acid constituents and that the acids enter into some form of combination with the basic chrome salts on the tanned fibres and produce a chrome soap, this insoluble soap being found in the interstices of the leather and producing a waterproof and pliable product. This theory is not sufficient to account for the differences produced by a hard and a soft soap just mentioned. If the above theory of the formation of a chrome soap be correct, the effects of a hard and a soft soap should be the same, since the chrome soap compound yielded by either kind is the same, whereas in practice a considerable difference in result is observed, the use of a hard or soda soap having the tendency to make the skin "cakey" when subjected to the pressure of the glazing machine. This chrome soap theory does not account for the fact that a soap and oil fat liquor is taken up by vegetable leather in which there is no possibility of the formation of a metallic soap such as a chrome soap.

Even with chrome leather in which it might be possible to have formed a chrome soap, no evidence of such is available. A chrome soap is soluble in certain solvents, but if a fat liquored chrome leather be washed in such a solvent no chrome soap is removed from the leather.

There are other arguments against the chrome soap theory. Thus if a fat liquored chrome leather be degreased by a suitable grease solvent, the final leather may be softer than before the grease has been removed. Of course if the leather had received no fat liquor at all it would not have been as soft as in either of the two cases. If it be argued that the grease solvent does not remove the chrome soap, which therefore is left to produce the softness, it can be answered that a similar effect may be produced by fat liquoring with an emulsion containing no soap, in which case there can be no formation of a chrome soap. The effect of a fat liquor is therefore either (1) that the leather removes the

soap and oil from the emulsion part of which is not removable by a grease solvent or (2) that the oil and soap produce a physical change in the fibre which is maintained even when the oil and soap are removed. This change in the fibre may be one of greater fineness of division.

Instead of using a separate soap and oil for making a fat liquor, some tanners use one oil and partly saponify it. Thus if an oil be taken and heated in a steam jacketed pan and alkali be added to it and the whole stirred, the oil will be converted into soap. If insufficient alkali be added to saponify the whole of the oil, some of the oil will be converted into soap and the remainder will remain in the oil state, so that a useful fat liquor can be made in this simple way.

Types of Fat Liquor

The commonest type of fat liquors is the one in which an oil is emulsified by means of a soap. Sometimes other additions are made for certain specific purposes. Thus it is common to add a small proportion of an alkali such as borax. Sometimes glycerine is also added and other substances such as flour may be added. The use and function of these materials will be dealt with later. Another quite distinct type and one which is becoming very common is the use of an oil which is emulsifiable without the addition of soap or special emulsifying agent. This type includes the so-called sulphonated oils and also one or two special types of oil of self-emulsifying properties. The sulphated oils have already been mentioned when dealing with the question of ease of penetration of oils. Both classes will be discussed later but at this juncture it may be mentioned that these emulsified oils are usually ordinary oils which have been chemically treated with sulphuric acid or other chemical substance, which treatment alters the character and composition of the oil in such a way that although they remain oily in appearance and feel, yet they mix or emulsify readily with water. The

introduction of these emulsifiable oils has opened up quite new methods and possibilities of fat liquoring. They may be used alone or along with other oils or even in conjunction with a combined oil and soap fat liquor. There are therefore many types of fat liquor possible and each type may now be considered more in detail.

Oil and Soap Fat Liquors

The emulsion produced when an oil is mixed with soap is still the commonest type of fat liquor, although recently the use of sulphated oils or acid fat liquors has reached very large proportions. As already mentioned, the choice of oils is a wide one and either a soft or a hard soap may be used. In either case the general methods of making up the emulsion are similar.

Methods of Making Oil and Soap Fat Liquors

The commonest and perhaps the best way of making an ordinary oil and soap fat liquor is to dissolve the soap in hot water and to add the oil in a fine stream or in small portions at a time to the hot soap solution stirring vigorously all the time. The stirring or agitation plays a very valuable part in emulsifying the oil. In most works where fat liquoring is at all widely practiced a special stirring apparatus or emulsifier is in use. This usually consists of a vessel shaped like an ordinary barrel but oval instead of round, standing on one end with the other end open. Two sets of revolving blades are placed in the vessel with the axles vertical and rotating in opposite directions so that a maximum agitation occurs. With a very good fat liquor an emulsion made in this way will remain stable for days without separating out, but where the fat liquor is made on the premises where it is to be used it is customary to prepare it immediately before use or at any rate to place it in the emulsifier before use, so that the particles of oil are very finely divided. If such additions as borax or flour are to be made they can be added to the

emulsifier during stirring. The main point to be observed is that the oil should be added to the hot soap solution and not the soap to the oil. If such an emulsifier as just described is not available a simple form of agitation can be made out of a cylindrical wooden vessel shaped like a drain pipe. A metal disc, perforated with holes, which just fits the inside of the vessel is provided with a wooden handle so that by pushing it up and down in the liquid in the vessel violent agitation is set up. The soap solution is poured in first and then oil is added in stages.

With fat liquors of the second type, that is made from the self-emulsifiable oils, the preparation is much more simple, and no special stirring apparatus is needed. By merely pouring these oils into water a stable emulsion is formed. Such a fat liquor need not therefore be prepared until the very moment it is required. This perhaps is one reason for the popularity of this class of fat liquor.

The following examples quoted by Lamb may serve as types of fat liquors:

I. For chrome calf:

1 gallon castor oil,
3½ lbs. soft soap,
½ lb. egg yolk.

II. For vegetable tanned calf:

2 gallons sod oil,
6 lbs. soft soap,
1 lb. egg yolk.

These quantities are for 300 to 400 lbs. of leather struck out ready for fat liquoring.

The soap is dissolved by boiling in as small a quantity of water as possible (one gallon of water to each 31 lbs. of soap may be taken as a standard). The oil is added to the hot soap solution, stirring all the time and the mixture boiled for a short

time. When the mixture has cooled down to below 100 degrees F. the egg yolk, first mixed with a little water is added. It is essential that the egg yolk be not added whilst the liquor is hot because it would be coagulated by the heat. Such a fat liquor should then be transferred to the agitator before use and warmed to the desired temperature. If the fat liquor contains no egg yolk the same care to avoid too high a temperature need not be exercised. Such a fat liquor may be made in bulk and stored in barrels and the correct quantity placed in the agitator at a time, or if the agitator is big enough the fat liquor may be made in it and measured quantities withdrawn from it as required.

With an oil and soap fat liquor containing no egg yolk, the soap should be dissolved in a small volume of boiling water and the oil poured in gradually, stirring vigorously all the time.

Both the above fat liquors contain egg yolk and are intended for high class goods. A type of a cheaper fat liquor suitable for chrome kip sides to be finished dull is as follows:

1½ gallons neatsfoot oil,
½ gallon sod oil,
2 oz. washing soda,
6 lbs. soft soap.

The actual process of fat liquoring is varied according to the class of leather. Thus with a chrome leather the temperature is generally higher than with vegetable leather. Also if dyed leather is to be fat liquored the procedure is different from when an undyed leather is to be fat liquored.

Fat liquoring is usually carried out in a drum and the best form of drum is that used for stuffing, that is, a hot air stuffing drum. It can be carried out in an ordinary drum but in this case some means such as the use of steam, must be provided for heating the drum. If a hot air drum be used the procedure is as follows: The drum is warmed to the required temperature by blowing in warm air, the goods to be fat liquored are then placed

in the drum and the whole turned until the goods themselves have reached the correct temperature. The fat liquor, also warmed to the correct temperature, is then run through the hollow axle whilst the drum is turning. In half an hour the whole of the fat liquor should have been absorbed by the leather but it is usual to continue the drumming for another ten or fifteen minutes. At the end of this time, the goods are removed from the drum and allowed to lie, preferably over night. Any liquid remaining in the drum should be clear as water.

By the use of a hot air stuffing drum, with a traveling thermometer it is possible to maintain and control the temperature of the goods at any desired point.

If an ordinary drum be used it is nothing like so easy to control the temperature, but the following may be adopted. The drum may be warmed by blowing in steam, the goods may be warmed by a previous immersion in warm water before placing them in the drum and the fat liquor then run in through the hollow axle. An alternative plan is to place the goods in the drum along with warm water and turn for a few minutes until warm, the water is then drained out of the drum by removing the pegs or by means of a skeleton door, and the warm fat liquor is run in through the hollow axle.

The maintaining of the temperature at the correct point is one of the most important features in successful fat liquoring, and a hot air drum is almost essential for good work.

The temperature should be the highest which is compatible with safety. There is no doubt that many of the failures to fat liquor chrome leather have been due to using too low a temperature.

With vegetable leather the temperature should not exceed 120°F. (50°C.) a more common temperature is 110°F. (44°C.) With chrome leather the temperature may go considerably higher, 140°F. (60°C.) being a suitable one, although much higher temperatures are safe.

The amount of fat liquor to be used depends on the character of the leather and the softness required. The volume of the liquor is also an important point. Most workers aim to keep the volume as small as possible, that is they keep the fat liquor as concentrated as possible, so that all that is left in the drum after fat liquor is a small pool of water. Some workers even squeeze the leather before fat liquoring and also use a very small volume of fat liquor so that the whole of it, that is, the oil, soap and water is taken up bodily by the leather. This plan certainly enables the fat liquor to be absorbed readily but it does not lead to uniform results. If the fat liquor be a good one and the condition of the goods be correct, for instance containing no free acid, and the temperature be right the leather should be capable of absorbing the oil from a fat liquor even when very dilute. When fat liquoring dyed leather it is often an advantage to keep the volume as small as possible to prevent an excessive bleeding of the color.

The Fat Liquoring of Dyed Leather

The fat liquoring of dyed leather is a much more delicate operation than that of an undyed leather because of the effect of the fat liquor upon the color dyestuff.

There are two alternatives, to fat liquor before dyeing or after dyeing.

There are difficulties by either plan. If the leather be first fat liquored there is a danger that the dyestuff will not strike the color readily or evenly, and unless the leather be very carefully fat liquored it is much more difficult to dye it than without the fat liquor. If the leather be dyed first and then fat liquored there is the danger that the color may be stripped by the fat liquor. The latter plan is the one usually adopted. In order to prevent the stripping of the color by the fat liquor, M. C. Lamb recommends the following plan: Add some of the fat liquor to a little of the partially exhausted dye bath or color the

fat liquor itself by the addition of a small quantity of dyestuff (previously dissolved) similar to that with which the goods have been dyed.

For fat liquoring dyed leather the fat liquor should be as neutral as possible in order to prevent stripping. When fat liquoring before dyeing it is essential that the whole of the emulsion should be taken up by the leather. If any oil be left on the surface of the leather the dyeing will be difficult and uneven. Something may be done to help in this direction by leaving the fat liquored goods in pile over a horse for several hours, preferably over night, before dyeing. This will enable the fat liquor to be very thoroughly and evenly absorbed by the leather.

Most of the difficulties which may arise in fat liquoring are more pronounced in the case of chrome leather than is the case of vegetable leather and it is much more difficult to fat liquor chrome leather than vegetable leather.

Most of the defects produced in the fat liquoring of chrome leather are due to the presence of free acid in the chrome leather which breaks up the emulsion and liberates the fatty acid from the soap as a sticky deposit on the grain.

All chrome leather when it is taken from the chrome liquors contains free acid. Most of this may be removed by washing with water but in order to remove the last traces it is necessary to use an alkali. This neutralization of chrome leather is therefore a most important step in the process. If too much free acid be present in the leather the soap of the fat liquor is broken down and the fatty acid is deposited on the grain. This will make dyeing both difficult and irregular and if the leather is to be finished with a bright surface it will make glazing difficult. Writing on this point, M. C. Lamb says, "It is generally admitted by those who are concerned with the manufacture of any kind of chrome leather that the fat liquoring operation presents more difficulties than perhaps any other process incidental to the manufacture of this difficult tannage. Indifferent and uneven col-

oring of colored leather; blotchiness usually taking the form of a map-like marking of a greasy nature often seen on black leathers; a white deposit appearing on storage of black leathers; a general "foulness" preventing the finishing of the goods to a nice, bright clean and clear finish; are a few but not all the defects which are only too commonly met with that have been brought about as the result of some treatment either before or during the fat liquoring process itself.

"Perhaps the most common defect met with is due to an incomplete absorption of the fat liquor by the skins, with the consequence that the goods when dry possess a slight greasy feel on the exterior usually accompanied by a more or less undertanned feeling of the skins themselves. This defect is brought about by indifferent absorption of the fat liquor with a consequence that the emulsified solution is deposited on the grain and flesh surfaces and does not penetrate through the leather, the goods in consequence being insufficiently nourished in the interior and possess an "undertanned feel" and the objectionable tinniness and "rattle" usually associated with this defect. One of the principal causes of this defect is due to the goods having been insufficiently neutralized by borax or other weak alkali preparatory to fat liquoring, the goods being subjected to the fat-liquoring process whilst in an acid condition. The acid in the leather has a detrimental effect upon soap and oil emulsions, causing a separation of the emulsion itself and acting upon the soap ingredients of the emulsion and liberating the fatty acids.

"It will be noted from the above how important is the operation of neutralizing the acids in the skins by treatment with alkaline solutions. When fat liquoring is attempted upon goods which have been insufficiently neutralized the emulsion is separated, as mentioned above, and will not penetrate into the interior of the leather, being merely deposited, as it were, on the outside surface. The object kept in view by the person in charge of the fat-liquoring operation is generally to take sufficient pre-

cautions to note that the goods are not rendered alkaline. When an excess of borax has been employed for neutralizing, the result upon the leather is to make it inclined to be thin and apparently under-tanned when a great excess has been used, or spongy and india rubber-like in character when the skins have been slightly over neutralized and rendered slightly alkaline, these defects being due to an alteration in the basicity of the chrome salt in the leather by the action of the alkali.

"It is usually the endeavor of the operator to leave the goods in a slightly acid condition, but unfortunately there is no simple means of ascertaining whether the acid in the skins has been sufficiently neutralized or not. The common test is to apply a piece of red or blue litmus paper to the cut surface of one of the thickest skins, but this test is not by any means a satisfactory one.

"The fact that when chrome leather has been neutralized and is left in a wet condition for any length of time dissociation of the chrome salts takes place in the fibre of the leather to such an extent that the goods again become acid in character, is often lost sight of by the foreman in charge of the goods. Skins which have been neutralized should be washed, dyed and fat liquored with as little delay as possible.

"The defect above mentioned of the skins when in a warehouse throwing off a white spue or deposit on the grain surface, particularly noticeable on black leathers, is chiefly due to this cause, the acid in the skins causing the neatsfoot oil and soap fat liquor to spue.

"When the goods are fat liquored before dyeing, any separation of the fat liquor brought about by acidity of the leather, or by the separation of the emulsified fat liquor itself, causing an uneven deposition and penetration of the liquor on and in the skins, will eventually cause an uneven dyeing effect.

"A leather which has been thoroughly fat liquored usually requires no special preparation before or after seasoning prepar-

atory to glazing. In the case of leathers which have been over-fat liquored and which in consequence have a tendency to greasiness on the grain surface, it is usually customary, in order to obtain a bright, clear glazed finish, to treat the leather with a weak acid solution; the acids usually employed for this purpose are formic, acetic or lactic to which a little bichromate of potash is sometimes added. Apparently this is the only known easy process which will satisfactorily overcome the "fouling" on the glazing machine of skins that have been indifferently treated in the fat liquoring process."

The Uses of Fat Liquoring

The advantages of fat liquoring over oiling have already been described and it should be obvious what are the main openings for the use of a fat liquor. There are two main types of use. (1) in which the fat liquor is given alone and which has as its object the incorporation of oil on the fibres to make the leather soft. (2) in which the fat liquor is used as an adjunct to some other process and in which it serves a subsidiary purpose. As an example of the former the case of chrome box calf may be taken. In this case the process of fat liquoring is the only means adopted to incorporate oil in the leather and is designed primarily for softness and to lubricate the fibres. As an example of the other class may be taken the use of a soluble oil to add to ordinary tan liquors in drum tannages, in which the function of the oil is to increase the penetration of the tannin to enable more weight to be absorbed without the leather being too harsh or cracky and to prevent damage to the grain of the leather by rubbing on the sides of the drum.

The Object of Free Alkali in a Fat Liquor

Many oil and soap fat liquors contain a proportion of an added alkali. The soap used almost always contains free alkali but in addition to this many workers use either borax or soda.

The object of the alkali is partly to increase the ease with which the oil is emulsified and to make the emulsion more stable and also partly to make allowance for any acidity which may be present in the leather to be fat liquored. Just as a soap and oil fat liquor is made less stable in the presence of acid so an excess of alkali makes the emulsion more permanent. The alkali is often added direct to the oil in order to "cut" it, that is in order that the oil when it is poured into the water may mix readily and not separate out.

Apart from helping the oil to be emulsified more readily the alkali is often added for another purpose, namely to overcome any acidity present in the leather. It is thought that if free alkali such as borax or soda be present in a fat liquor, any acid in the leather will first neutralize the free alkali before it will affect the soap or destroy the emulsion.

In this sense the addition of a free alkali to a fat liquor may be regarded as a safety trap for any free acid present in the leather.

If alkali is added for this purpose it should be added immediately before the fat liquor is to be used. Sometimes it is added as the fat liquor is being made or the fat liquor with the added alkali may be kept in the agitator for hours or days before being used and at an elevated temperature. If the alkali be kept in contact with a saponifiable oil such as neatsfoot, castor or cod for any length of time, particularly if warm, the alkali will saponify some of the oil. By so doing the oil is converted into soap and if a great excess of alkali has been added the whole of the oil may become converted into soap. Thus the composition of the fat liquor may undergo a profound change. The proportion of oil will diminish and that of soap will increase. The alkali itself will be used up so that the direct object of the alkali, that of neutralizing any free acidity in the leather cannot be achieved.

Disadvantages of Alkaline Fat Liquor

For most purposes a neutral fat liquor is to be preferred to an alkaline one. If the leather cannot be sufficiently freed from acid to render it possible to fat liquor successfully with a neutral fat liquor, that is without the addition of free alkali, it would be better either to devise better means of neutralizing the acidity of the leather or to use a sulphated oil or acid fat liquor. The free alkali may produce undesirable effects in addition to overcoming the free acid in the leather. There are two disadvantages of the alkaline fat liquor, one is the removal of tan and the other is the stripping of dyestuff.

Ordinary vegetable tanned leather whilst very resistant to the action of water is readily attacked by alkalies. It can be washed with water and still retain its leather properties, but alkalies will remove or strip the combined tanning matters from the fibres and so destroy the leather properties. If a lightly tanned vegetable leather, therefore, be fat liquored with an emulsion containing free alkali some of the tannin will be removed and the quality of the leather will be spoiled.

If such a fat liquor be given to dyed goods, and it is more common to fat liquor after dyeing than before, there will be tendency for the alkali to strip some of the color from the leather. There is, therefore, not only a loss of dyestuff but lack of uniformity is also produced.

Leather for fancy and delicate shades is therefore usually fat liquored with a fat liquor made as neutral as possible, that is, made from a pure oil and a neutral soap. M. C. Lamb, writing on this point, says, "The solution to be used must be a perfect emulsion, and it is advisable, if the same is to be used on leather tc be dyed in any other color than black, that the emulsion should be quite neutral in character and not in the least degree alkaline. An alkaline fat liquor such as is often prepared by the addition of a small quantity of washing soda or other alkali to the oil and soap mixture, is never to be recommended; such a fat

liquor will invariably strip the color from a dyed leather, and moreover does not possess the nourishing properties of the neutral solution."

Sulphonated Oils

Some of the uses of sulphonated, or perhaps more correctly, sulphated, oils have already been described and before proceeding further it might be well to describe more in detail the nature of these oils, as there is a widespread ignorance of their true character. Most users know that they are oils which have been treated with sulphuric acid and in many cases it has been a question of a little learning being a dangerous thing. Knowing the injurious action of sulphuric acid upon leather and knowing what care must be taken to remove all traces of sulphuric acid from tanned leather in order to avoid the rotting effect on the fibre, some leather manufacturers have fought shy of a sulphated oil in the fear that the sulphuric acid contained in it might cause damage to the leather.

This is quite an unjustifiable fear. The sulphuric acid in a sulphated oil should be no more in evidence or injurious to leather than the sulphuric acid in sodium sulphate is in evidence.

A correctly sulphated oil contains no free sulphuric acid and has no disintegrating action upon leather.

Perhaps the question would be simplified by considering the way in which one of these oils is made. The best known, the earliest and the one most widely used in connection with leather is sulphated castor oil or Turkey Red Oil. The following method is one described by Salamon and Seaber.

About 35 lbs. of castor oil at a temperature of about 50 degrees Fahrenheit is poured into a wooden or galvanized vessel and 8 lbs. of sulphuric acid added very slowly, keeping the oil in motion during the addition, and cooling if necessary. The acid should be added very carefully so that the temperature is kept low, and when it has all been added, the whole should be stirred

vigorously for a considerable time, covered and allowed to stand for two or three days.

If a small portion is largely diluted with water and a few drops of ammonia are added a clear solution should result. If this is not the case, however, add a little more sulphuric acid (up to 1 or 1½ lbs.), but usually it is not necessary. Wash with an equal volume of water, stand till the oil comes to the top and siphon off the water. Repeat this twice and then add 5 ozs. of concentrated ammonia and stir thoroughly.

The sulphuric acid enters integrally into the oil molecule and does not exist in the free state. The finished product appears oily, is oily to the touch and produces the same effects as an ordinary oil when applied to leather. That is, it lubricates the fibres and renders the leather supple. It differs from an ordinary oil in that it emulsifies with water without the addition of soap or alkali. If slightly alkaline it dissolves in water to give a clear transparent solution. If made slightly acid it will still remain emulsified without separating from the water. This is where the great advantage of sulphonated oils arises. They can be used along with materials which are acid in character. Thus they can be used as an addition to ordinary vegetable tan liquors to facilitate penetration and to give weight. An ordinary oil and soap fat liquor would be useless in this case. Similarly in the fat liquoring of chrome leather. Chrome leather after tanning is always acid in character and great pains are taken to remove as much of this free acid as possible before the finishing processes. The methods adopted may be either a thorough rinsing with water or a washing treatment with alkali. It is very difficult just to remove the whole of the free acid without over-stepping the mark and making the leather alkaline. For efficient fat liquoring so that no trouble shall arise in subsequent processes of finishing such as glazing it is essential to remove this free acid if the fat liquoring is to be carried out with a soap and oil fat liquor.

The acid present in the leather reacts with the soap of the fat liquor to form a free fatty acid, which is not soluble but a waxy substance. This separates out on the surface of the leather as a sticky substance, so that not only is the leather not properly nourished but its appearance is spoiled and it is the cause of faulty uneven dyeing and of difficulty in glazing.

„ With a sulphated oil on the other hand which is stable in the presence of acid there is no separation of free fatty acid, there is not the same difficulty in glazing or uniform dyeing and the leather need not be so carefully neutralized. It tends to make the processes of finishing chrome leather much more fool-proof. The great advantage therefore of the use of a sulphated oil over an ordinary oil and soap fat liquor is that the presence of acidity does not interfere with the success of the process.

Another great advantage is that it acts as an emulsifying agent upon other oils. An ordinary oil mixed with a sulphated oil will give a stable emulsion so that the sulphated oil may take the place of soap in an ordinary fat liquor. Although soap does serve a purpose in fat liquoring, apart from its use in emulsifying the oil, as will be explained later, yet for many purposes these effects of the soap are not necessary and a sulphated oil can therefore take the place of the soap. It is usually the soap which is the direct or indirect cause of any fault produced in fat liquoring, so that by using a sulphated oil instead of a soap for producing the emulsion many troubles may be overcome.

A sulphated oil alone is usually not employed for fat liquoring except in the cheaper classes of goods. It is thought not to give sufficient body or substance to the leather. It finds its greatest use in conjunction with other oils.

Thuau has given the following recipes using sulphated oil as an emulsifying agent for other oils:—

	Parts
(1) Sulphated Castor Oil (50 per cent water)	40
Mineral Oil	23

	Neatsfoot Oil	37
(2)	Sulphated Castor Oil	15
	Colza Oil	15
	Mineral Oil	30
(3)	Sulphated Castor Oil	15
	Cod Liver Oil	20
	Mineral Oil	25

It will be noticed that each formula includes the use of mineral oil. According to Thuau the emulsions made from a sulphated oil and an oil such as neatsfoot are not stable but that the addition of a sufficient percentage of mineral oil makes the emulsion perfectly stable. When making emulsions of this type the sulphated oil and the mineral oil are first mixed and the neatsfoot or cod oil added to the mixture with constant stirring.

Other oils besides castor oil are now sulphated. The commonest are neatsfoot and cod oils. Many so-called soluble oils are now put on the market for tanners' use with special names which have no bearing on the origin of the oil. These oils are not soluble in the sense that they dissolve in water to give a clear solution, they are more correctly called emulsifiable oils. Most of them are compounded of a sulphated oil and some other cheaper oil. Thus some are evidently mixtures of equal parts of sulphated cod or castor oil and mineral oil. Sometimes the percentage of mineral oil in these "soluble" oils reaches as high as 80. When considering the price of these emulsifiable oils, the percentage of mineral oil should be taken into account and it may often be found that it would be cheaper to buy the straight sulphated oil and mix it with the other oils such as mineral.

Perhaps a word of caution might be interposed here with respect to the estimation of mineral oil in soluble or emulsifiable oils. A genuine sulphonated castor oil is completely saponified by boiling with alkali so that it contains no unsaponifiable matter. The presence of unsaponifiable matter in an ordinary oil

such as cod, castor, neatsfoot or olive is usually taken to be evidence of adulteration with mineral oil. A sulphonated oil is, however, often mixed with substances which are unsaponifiable but which are not mineral oils. Thus, according to Alan Claflin, some of the best fat liquors ever devised for leather making are made by mixing a sulphonated oil with a distilled oleine. The distilled oleine is made by distilling under pressure with superheated steam, greases or oils which are recovered as by-products, for example from wool washing. Oleines produced in this way from miscellaneous recovered greases contain a large proportion of unsaponifiable matter which is not mineral oil and which has not the properties of mineral oil. A commercial fat liquor therefore may be reported upon analysis as containing mineral oil when it really only contains a distilled oleine.

The ease with which a sulphonated oil will emulsify another oil depends largely upon the condition of the latter. Thus an oil which has stood a long time or which has become rancid will emulsify much more readily than a fresh neutral oil. Thus before the process of sulphonating castor oil was discovered, rancid olive oil was used for the same purpose as Turkey red oil or sulphonated castor oil. Olive oil becomes rancid much more rapidly than castor oil and commercial samples almost always contain free fatty acids, some samples containing up to 50 per cent. This high proportion of fatty acids renders the emulsification much easier, and for use as Turkey red oil the oil is allowed to ferment and become rancid. Such an olive oil for use as Turkey red oil should contain 25 per cent of fatty acids. The sulphonation of other oils is not quite the same as of castor oil. With the latter the sulphuric acid is taken up integrally by the oil, in other words the sulphuric acid and the oil form an additive compound. With a correctly sulphonated castor oil the product is soluble in water to a clear solution especially if made slightly alkaline and diluted, if not clear it is a sign that the reaction has not proceeded normally or that other oils have been

added. With other oils the product does not dissolve in water to a clear solution and the reaction between the oil and the sulphuric acid is not quite the same. The sulphuric acid, instead of forming an addition compound with the oil, may break up the oil into free fatty acid and combine with the glycerine. Such an oil may be easily emulsified and yet be quite different from a sulphated castor oil. It probably owes its high emulsifying properties to its similarity to a rancid oil which is explained elsewhere in this article is much more easily emulsified than a neutral oil. The fatty acid itself and the compound of the sulphuric acid with the glycerine helps to make emulsification easy.

Such a sulphonated oil although easily emulsified does not behave in the same way as a sulphonated castor oil. It may give more body to the leather but it possesses the drawback of not being so resistant to the influence of acid in the leather. If the fatty acid be neutralized with soda or ammonia the material will contain soap and the resulting fat liquor will possess some of the disadvantages of an ordinary soap and oil fat liquor.

Not only can sulphonated oils be used for fat liquoring but they can also be used in conjunction with the dyeing or retanning processes. Thus instead of giving separate processes for fat liquoring and dyeing as is the case when using a soap and oil fat liquor, the two may be merged into one. Similarly when retanning such things as East Indian tanned kips with gambier, sumach or other extract, it is possible to mix a sulphonated oil with the tanning material, to save a process and also to increase the penetration of the tannin. It is even possible to tan, dye and fat liquor in one process, although this should be regarded more as a freak performance than as usual practice.

Sulphonated oils either alone or in conjunction with mineral oil are largely used in ordinary vegetable drum tanning. The use of the drum for tanning is rapidly increasing, particularly for the tannage of bellies and shoulders. Sulphated oils may be used in this case with two objects in view. In the first place the

presence of oil in the tan liquor helps the latter to penetrate the leather, so that tannage is made more rapid, one of the objects of drum tanning. The oil also helps to prevent damage to the grain of the leather by the action of the drum. Heavy leather particularly is apt to lie in folds in the drum. If such folds are allowed to remain, the constant friction of leather against the drum will in time cause the grain of the leather to be worn away. The presence of a sulphated oil together with a mineral oil helps to lubricate the external parts of the leather and prevents damage by rubbing of the grain against the sides of the drum.

The presence of the sulphonated oil in the leather also helps to prevent crackiness or brittleness. One of the great disadvantages of rapid tanning processes such as drum tanning against a slow pit tannage is that by the former process the leather is inclined to crack and be brittle. This is possibly due to the greater weights which are obtained and also perhaps to the fact that pelt for drum tanning is often more strongly acid swollen before tanning than for ordinary tanning. By the penetration of a thin film of oil through the fibres the latter are allowed to move over one another more freely so that brittleness is overcome. This function of a sulphonated oil also applies to any leather which is inclined to be brittle. The effect is somewhat similar to that produced in leather by certain hygroscopic materials such as glycerine, glucose or certain inorganic salts which are often used for weighting leather. These materials often make a leather softer, mellower and less inclined to be brittle but they do it by attracting moisture. They must of course be regarded as weighting materials and they also possess the disadvantage of being washed out by water. A sulphonated oil on the other hand is not removed by water and it does not depend, for its mellowing properties, upon its attraction for moisture but upon its lubricating properties. A leather made mellow by means of a sulphonated oil does not contain more than a nominal quantity of moisture so that it retains its mellow-

[illegible] almost indefinitely. A leather made mellow on the other [illegible] of a hygroscopic material would probably become [illegible] the moisture were removed.

[illegible] leather made mellow by a hygroscopic material and [illegible] damp climate and then transferred to a warm [illegible] be quite altered in character.

[illegible] of a sulphonated oil in drum tanning or in [illegible] lighten the color. This is brought about by pre- [illegible] uncombined tannin from coming to the surface dur- [illegible] similar to the effect, already discussed, of [illegible] to the surface of leather before drying.

[illegible] used as an addition to the tan liquors in [illegible] accompanied by another oil such as mineral [illegible] amount of the sulphonated oil may be only a [illegible] the accompanying oil. For instance, Thuau [illegible] for the addition to tan liquors the [illegible] 500 lbs. of strong liquor, 20 lbs. of min- [illegible] sulphonated castor oil.

[illegible] the use of sulphonated castor oil to the [illegible] softening and glassing before drying to pre- [illegible] and the uncombined tannin from [illegible] and darkening the color of the grain.

The Use of Amides

[illegible] emulsifying agent for which large claims have been [illegible] material similar to a sulphonated oil is the [illegible] which are typified by stearamide. These [illegible] are the amides of the fatty acids. Thus stear- [illegible] amide of stearic acid, has the formula $C^{17}H^{35}CONH^2$, [illegible] is a stearic acid in which OH has been replaced by [illegible]

[illegible] substance is akin to the constituent of egg yolk which [illegible] latter such a fine emulsion. The oil in egg yolk is [illegible] olive oil but in addition there is a small quantity

of material called lecithin which allows the oil to be finely and permanently emulsified. The lecithin is a complex body containing fatty acids such as stearic and palmitic, in combination with cholin and glycero-phosphoric acid. This lecithin enables the oil to be emulsified and also serves as nourishment for the leather. It is claimed for these fatty acid amides that they are similar in composition and effect to the lecithin in egg yolk. Egg yolk is perhaps one of the finest emulsions available for leather but owing to its high price it is only used for the highest class of goods. Many workers, however, always think the presence of a small quantity of egg yolk is worth while in any fat liquor and many recipes contain small proportions of egg yolk. The makers of stearamide claim that its action is similar to that of the lecithin in egg yolk. "The amides of the higher fatty acids of which stearamide is a typical example have the peculiarity, the same as the physiological amides like lecithin, tyrosin, etc., of remaining suspended in minute division in watery solution, and the power of lastingly emulgating considerable proportions of neutral oil and fats. Thus stearamide boiled up with a very small quantity of soap to act as a protective colloid keeps in emulsion not only from five to fifteen times its own weight of such oils as neatsfoot, degras, fish oil and other oils commonly used in the leather trade but in addition is capable of producing fine emulsions of substances that formerly could not be practically emulsified, such as tallow, some mineral oils and paraffin wax."

Pure stearamide is a snow white crystalline body and glossy like mother of pearl. It resists acids and alkalies to a great extent and is like the waxes in that it is indifferent to most other chemicals. An emulsion made from stearamide and another oil is stable unless crystalloids such as sodium sulphate are present where the amide and the oil rise together to the surface.

Commercial fat liquors are now on the market made with stearamide as the base. Thus to substitute egg yolk a mixture is

made of stearamide and oil in the same proportions as lecithin and oil are present in egg yolk.

So called soluble or self emulsifiable oils are sometimes placed on the market which are really nothing else than strong soap solutions with perhaps an addition of some oil. Such a mixture will produce emulsions with other oils in the same way as a sulphonated oil will, but the result is very different. The sulphonated oil will produce an emulsion which is stable in presence of acids, it contains no soap and will not be thrown out by traces of acid. A fat liquor made from a soluble oil which is nothing but soap and oil will not differ from an ordinary soap and oil fat liquor and will possess all the disadvantages of a soap fat-liquor.

Buyers of soluble oils should be on their guard against tricks of this sort and should get a statement of the composition of the material.

Emulsions Made With Oil Solvents

Another type of emulsion quite distinct from those already described is based on the emulsifying properties of an oil solvent. Instead of using soap to emulsify the oil some substance in which the oil is soluble is used. The solvents which may be used include any of the common ones, such as alcohol, benzene, carbon bisulphide, carbon tetrachloride, or even some of the more recent non-inflammable solvents such as ethylene trichloride.

Thuau describes a method of making such an emulsion thus:

	Per cent
Water	50
Alcohol	10
Ammonia	5
Neatsfoot Oil	10
Oleic Acid	25
	100

The alcohol and the oleic acid are mixed and the ammonia and a little water added whilst stirring. The neatsfoot oil is then added and finally the remainder of the water. It is also possible by this method of emulsification to incorporate in the emulsion insoluble solids. For instance, it is possible to incorporate 30 per cent of mineral matter, finely powdered silicates in a mixture of oleic acid, alcohol, ammonia, benzene and water.

Such types of emulsion are more of academic than practical interest. Their cost would be prohibitive and they are never likely to replace the commoner types of fat liquor except for very special purposes.

Still another type of emulsion which may be used upon leather is the one prepared by mixing a sulphonated oil such as Turkey red oil with an oil or a fatty acid dissolved in an oil solvent. If a fatty acid be dissolved in a solvent such as benzene or carbon tetrachloride and then sulphonated oil be added, the product will give a stable emulsion when added to water. This property can be used for another process, that of removing the grease from goods in the wet state. In many cases it is extremely useful to be able to degrease in aqueous solution. Thus with skins in the pelt form, it would be much more convenient to be able to remove the grease by a material in an aqueous solution or emulsion than having to dry them and then degrease in an ordinary degreasing plant. Something in this direction can be done by means of a mixture of a sulphonated oil and a grease solvent such as carbon tetrachloride. Such a mixture will emulsify with water and the emulsion so formed can be used for degreasing wet skins or leather. The process involves no special plant for it can be done in an ordinary drum, and if carbon tetrachloride or one of the newer solvents such as trichlorethylene be used there is no fire risk as the material is not inflammable.

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